# MONITORING OF MUTAGENS AND CARCINOGENS IN COMMUNITY AIR

Contract No. ARB A1-029-32
Final Report
May 1984

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# SUMMARY OF FINDINGS

*Analyses of mutagenicity, air quality and meteorological measurements made between 1979 and 1982 in Contra Costa County yielded the following conclusions:*

1. *A major portion of the mutagenicity of Contra Costa aerosols that were collected during August and October 1981 pollution episodes could be accounted for by the variability in the fine-fraction lead concentration in these aerosols. This observation suggests that during the summer and fall episodes the majority of the mutagenicity was due to vehicular emissions. The correlation between mutagenicity and fine-fraction lead during the winter episode in January 1982 was lower than during the summer or fall episodes. This suggests that during the winter episode vehicular emissions contributed proportionally less to mutagenicity than during the summer and fall episodes.*

2. *During the three 1981-82 episodes, no evidence that refineries contributed to aerosol mutagens was found. Nickel is a tracer for fuel oil combustion and refinery operation. No significant statistical relationship was found between nickel and aerosol mutagenicity. The monitoring site at Martinez, which is in close proximity to several refineries, experienced the highest average concentrations of nickel and the lowest average aerosol mutagenic densities.*

3. *The source pattern during the January 1982 winter episode was the most complex, and the measurements indicated unidentified sources of wintertime mutagens. Qualitative results suggested possible contributions of residential wood combustion to polycyclic aromatic hydrocarbons (PAH) during the winter.*

4. *Genetic evidence suggests that nitroarenes (nitro-substituted PAH) may have accounted for one-half or more of the observed direct-acting mutagenic density during pollution episodes. This is based on the observation that mutagenicities of most aerosol extracts were at least a factor or two lower in a nitroreductase-deficient strain of Salmonella (TA98NR) than in the parent strain (TA98).*

5. *Mutagenicity and PAH concentrations in four-month composites showed marked seasonal variations. Between November 1979 and June 1982, levels measured in the winter (November-Febraury) were five to ten times higher than those*

*measured in the spring (March-June). Levels during the summer (July-October) were intermediate.*

6.     *Annual average concentrations of mutagenicity and PAH did not change significantly over the period between November 1979 and June 1982.*

# ACKNOWLEDGMENTS

# ABSTRACT

This field and laboratory study has measured the mutagenic activity of ambient air particulate extracts collected in Contra Costa County, California, identified and quantitated a number of specific organic compounds which contribute to the mutagenicity and determined the major contributing sources. Intensive air sampling for source identification was carried out at four locations (Pittsburg, Richmond, Concord and Martinez) during seasonal pollution episodes. Sampling was done over 36-hour periods in August and October 1981 and in January 1982. Organic extracts of air particulate matter were analyzed for mutagenic activity in the Ames <u>Salmonella</u> test and for selected polycyclic aromatic hydrocarbons (PAH) by high pressure liquid chromatogaphy (HPLC) coupled with fluorescence detection. Ames testing was performed with and without added rat liver (S9) extract in order to measure both indirect (+S9) and direct-acting (-S9) mutagens. Nine polycyclic hydrocarbons were identified by HPLC and their sum used as a surrogate for total PAH. Air samples were also analyzed for trace metals (including Pb, Ni and Fe), secondary particulates ($NO_3^-$ and $SO_4^=$) and pollutant gases ($O_3$, CO, NO, $NO_2$, $SO_2$). Multivariate statistical techniques were used to provide insights to sources of mutagens and PAH. Factor analysis helped identify types of emission sources and select source tracers. Using tracers for automobiles (Pb,), industry (Ni,) crustal material (Fe), secondary aerosols $NO_3^-$, $SO_4^=$ linear regression models were developed of the form Mutagenicity = a (Pb) + b($NO_3^-$) + . . . where a and b were the regression coefficients determined from data collected during intensive sampling episodes.

The results suggested the following interpretation: During the August episode, automobile-related pollutants accounted for 60-70 percent of the mutagenicity (indirect and direct) and the PAH. About one third of the mutagenicity was attributed to nitrate-associated secondary aerosols; however this conclusion is based on uncertain $NO_3^-$ measurements and is therefore not very firm. During the October episode, automotive sources accounted for essentially all of the indirect- and half of the direct-acting mutagenic activity, as well as more than half of the PAH. Sulfate-associated secondary sources contributed the other half of the direct-acting mutagenicity. Industrial (Ni-associated) sources added about one-fifth of the PAH and about 20 percent of the PAH could not be accounted for. The sources pattern during the January episode was very complex and quantitative source apportionment was not successful. However qualitative results suggested contributions to mutagenicity from

vehicular traffic and contributions of residential wood combustion to PAH during the winter.

Chronic air sampling for seasonal variations and trends was also carried as part of the study. Twenty-four hour hi-vol samples were collected in Contra Costa every sixth day between November 1979 and June 1982 and four-month seasonal composites prepared and analyzed for mutagenic activity, PAH and other particulate pollutants. Mutagen and PAH concentrations showed dramatic seasonal variations and were highest in the winter months (November - February). No annual trends in levels of mutagens, PAH and other pollutants, were apparent over the 32-month study period.

Information was obtained about the nature of the chemicals which contribute to the mutagenic activity of air particulate extracts. Contra Costa aerosol extracts contained both direct-acting and indirect-acting mutagens. Direct-acting mutagens predominated during warm-weather months, while both types were significant contributors during cold-weather months. Polycyclic aromatic hydrocarbons were among the indirect-acting mutagens found. However, the nine polycyclic hydrocarbon species measured accounted for only a small amount (ca. 1%) of the observed mutagenic activity. Indirect measurements in bacterial nitroreductase-deficient mutants suggested that nitroorganic compounds (e.g. highly mutagenic $NO_2PAH$) may contribute half of the mutagenic activity of aerosol extracts. Direct chemical identification and quantitation of these compounds in Contra Costa air remains for future research.

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## I. INTRODUCTION

### A. Objectives of the Study

The objectives of ARB Agreement A1-029-32 are:

1. To refine and standardize chemical and microbiological methods for determining the concentrations of selected mutagens and carcinogens in ambient community air particulate material.

2. To better determine the sources and chemical identities of mutagens and carcinogens in Contra Costa County community air.

3. To expand the community air mutagen-carcinogen data base for further integration with the epidemiological cancer studies in Contra Costa County and elsewhere.

### B. Background

#### The Work in Perspective

Research conducted over the past four decades has revealed the presence of a variety of chemical carcinogens in solvent extracts of community air particles (1). However, the presence of these chemicals, at the concentrations typically found in ambient air, constitutes a public health risk of uncertain magnitude (2).

As early as 1942, Leiter, Shimkin and Shear (3) reported the experimental production of tumors in animals using tars from city air dusts. Connective tissue tumors (sarcomas) were induced in mice following the injection of extracts of atmospheric particles collected in several eastern U.S. cities. In the early 1950s, Kotin and co-workers (4) demonstrated that carcinogenic aromatic hydrocarbons, including benz(a) pyrene (BAP), were present in Los Angeles air and that atmospheric extracts were carcinogenic to animals in the laboratory. Soon after, Sawicki and co-workers (5) measured BAP and other carcinogenic polycyclic aromatic hydrocarbons (PAH) in the air of

more than two dozen American cities. BAP concentrations as high as 30 ng/m$^3$ were found in air particulate samples collected in Los Angeles during 1958-59; the annual average for the same period was 3 ng/m$^3$. Since that time BAP concentrations have decreased significantly in California and elsewhere (2,6). Until recently, research on carcinogens in community air particles has focused primarily on BAP and certain other carcinogenic PAH; however these compounds do not account for most of the carcinogenic activity of aerosol extracts. There must be other compounds which account for the "excess carcinogenicity" of ambient air extracts (7). Therefore, the decrease in BAP over the past twenty years does not necessarily represent a significant reduction in the potential cancer hazard.

## Air Particulate Mutagens

The recent development by Ames et al (8) of the Salmonella mutagenicity test has revolutionized environmental carcinogen testing. Because most chemicals that are carcinogenic in animals are also mutagenic in bacteria, the Ames test in practice is a good predictor of carcinogenic potential (9). Soon after introduction of the Ames test in 1975, Pitts et al (10), Talcott and Wei (11) and Tokiwa et al (12) successfully applied it to community air particles and demonstrated mutagenic activity in aerosol extracts. Research in this field has accelerated rapidly since then and we now know that chemical mutagens, as well as carcinogens, are ubiquitous components of the urban atmosphere in California and elsewhere (13-19).

Compounds of particular concern are those found in particulate polycyclic organic matter (POM). Mutagens in POM include certain unsubstituted PAH such as BAP and benz(a)anthracene (BAA). However these PAH constitute only a small fraction of the observed mutagenicity of POM. Furthermore a major proportion of the mutagenicity in ambient POM extracts is due to direct-acting mutagens which do not require metabolic activation; the PAH require prior metabolic transformation to become active mutagens. Recent studies have focused on highly mutagenic nitrosubstituted PAH (nitroarenes) such as nitropyrenes, which are direct acting mutagens. Nitroarenes have been detected in diesel exhaust (20) and urban air (21,22).

It is important to assess the total mutagenic and carcinogenic potential of ambient air POM, especially as new and expanded energy technologies are introduced in California. One way, at least in theory would be to measure all the mutagens and carcinogens in POM. However, chemical methods are not now available which can detect all such compounds in complex mixtures. Further, even such exhaustive compilations would neglect synergistic and antagonistic effects. Fortunately, the Ames test has made this assessment task more tractable because it is a good predictor of the carcinogenicity (9).

## Problems of Complex Environmental Mixtures

Several additional problems arise when considering complex mixtures. First of all adequate validation of the Ames test for mixtures had not been done even though the test has been widely applied to environmental mixtures and body fluids. These include air, water, cigarette smoke, auto exhaust, foods, drugs and urine (23).

Another problem in applying the Ames test to ambient air mixtures is that organic extracts of air particulates are significantly more mutagenic than predicted on the basis of the amounts of the known chemical mutagens present (24). Thus, there remains an "excess mutagenicity", as determined by the Ames test, which requires chemical description. The usefulness of the Ames test, as a predictor of potential health hazards will be enhanced if the disparity between observed and predicted mutagenicity can be lessened. Therefore, it is advantageous to use both the Ames test and chemical characterization together in attempting to assess the potential carcinogenic effects of ambient air particulate matter (16,17,24).

## Epidemiological Studies with the Ames Test

Although not a quantitative test in the sense of having a well-established accuracy, the Ames bioassay yields results which indicate relative mutagenicity. Thus, it has been considered appropriate for use in monitoring ambient air for relative mutagenicity and potential carcinogenicity. The results have been used as a key environmental measurement in epidemio-

logical studies attempting to relate cancer and air pollution (16,17). Results obtained by AIHL using the Ames test were an integral part of the recent Contra Costa County Cancer Study (6). In the study, measurements of airborne mutagens, selected PAH and other chemical pollutants were integrated with lung cancer incidence data. The geographic distribution of mutagenicity was not associated with the distribution of lung cancer, with one exception, viz. sulfate. However the correlation with $SO_4^=$ was significant only in males and disappeared when socio-economic status was factored in. Subsequently a case-control analysis established that smoking, not environmental or occupational hazards, was responsible for the high rate of lung cancer among male blue-collar workers in Contra Costa County (6). Thus, the relatively insensitive tools of epidemiology did not detect an impact of community air pollution on the incidence of lung cancer. The lack of epidemiological sensitivity should not obscure the fact that many mutagens and carcinogens are present in community air particles.

## Routine Air Monitoring

Before the Ames test can be used for general monitoring of ambient air quality there are a number of technical problems that must be addressed. The ambient air work done up to the present time using the Ames test has been carried out in a research format and the field work has usually been carried out independently of any existing monitoring networks. The laboratory procedures have involved many separate determinations per sample. Consequently both the collection and laboratory procedures are relatively expensive either for routine or special purpose monitoring applications. There is a need for continued refinement and standardization of these procedures so that field collection and laboratory porcedures are more routinized and less expensive.

## Sources of Airborne Mutagens

Another fundamental problem concerns source identification. The measure of relatively high mutagenicity in a given geographical area is of limited value unless the major sources of the mutagenicity can be identified and therefore potentially controlled. The integrated use of chemical and bio-

chemical data is of special value for this complex problem. There are indications that some of the elements (e.g., Pb,V) and PAH ratios (e.g., benzo(a)pyrene/benzo(ghi)perylene (BGP)) can be used as tracers for various pollution sources. For example, earlier studies (1,16) have shown that power plant and petroleum refinery emissions have higher BAP/BGP ratios than auto emissions.

In the previous, Contra Costa air pollution study mutagenicity, organic and inorganic chemicals and gaseous pollutants were measured (16, 17). We sampled every sixth day for one year (1978-79) at 14 Contra Costa locations and concluded that mobile sources were undoubtedly significant contributors to carcinogenic PAH. However more research was needed to define the major sources of particulate mutagens. The present study attempts to address this problem of mutagenic sources.

Further research is also needed to understand the "excess mutagencicity" problem. Much current research is focused on identification of nitro-substituted PAH which may contribute significantly to the mutagenicity. Although easy to form, they are difficult to detect chemically (25-27). Recently new strains of Salmonella have been developed that are deficient in nitroreductase activity (28,29), which allow them to be used as approximate "indicators" of mutagenic nitro-PAH in air samples. In the present work one of these strains TA98NR was incorporated into the Ames bioassay test in order to make the test not only a general predictor of genotoxicity but also an improved indicator of nitroorganics which might be causing some of the mutagenicity observed.

C.    Major Findings of This Study

Progress was made in four areas of investigation: development of methods and standards for measuring mutagens and carcinogens; identification of sources of particulate mutagens and carcinogens; identification of mutagenic and carcinogenic compounds in air particle extracts; analysis of seasonal variations and trends in levels of mutagens and carcinogens in Contra Costa community air.

1.    Methods and standards developments

   a)    A modification of the Ames bioassay with increased sensitivity for mutagens was applied to the analysis of air particle extracts. Measurements of mutagenicity were obtained using air samples collected every two hours. The increased sensitivity will allow diurnal pattern measurements, an important technique for assessing sources of mutagens.

   b)    Novel nitroarene standards were synthesized and characterized. Unusually high mutagenicities of dinitrobenzo(ghi)perylenes and S-9 dependence for mononitrobenzo(ghi)perylene and mononitro coronene were observed in the Ames Salmonella assay. These compounds may be found in vehicle exhaust and the atmosphere.

   c)    A method for routine separation, identification and quantitation of specific polycyclic organic molecules in ambient air extracts was perfected. The method does not require sample prefractionation or clean-up and employs high pressure liquid chromatography (HPLC) coupled with fluorescence detection.

2.    Mutagen and carcinogen source identification.

   a)    It is feasible to use multivariate statistical techniques to identify types of air pollution sources and to apportion the contributions of these source-types to the mutagenicity and PAH in aerosols collected during pollution episodes.

   b)    Source patterns during pollution episodes were different. During summer and fall episodes, vehicular emissions accounted for most of the mutagenicity and PAH measured. During a winter episode vehicular emissions again contributed to mutagenicity. However the vehicular contribution was lower. Possible contributions of residential wood combustion to PAH were also noted.

3.  Chemical identification of mutagenic and carcinogenic compounds in air particle extracts.

    a)  Eight unsubstituted PAH, including BAP and other carcinogens, and one oxygenated-PAH, benzanthrone (BO), were identified and quantified in air particle extracts. These compounds accounted for only about one percent or less of the total indirect (S9-dependant) mutagenicity of extracts from pollution episodes.

    b)  Biochemical evidence suggests that nitroarenes may account for one-half or more of the observed direct-acting mutagenicity during pollution episodes. This is based on the observation that mutagenicities of most extracts were at least a factor of two lower in a nitroreductase-deficient strain of Salmonella (TA98NR) than in the parental strain (TA98). The nitroreductase is required for mutagenic activation of many nitroarenes.

4.  Analysis of seasonal and annual trends.

    a)  Mutagenicity and PAH concentrations in 4-month composites showed dramatic seasonal variations. Levels measured in the winter (November - February) were five to ten times higher than those measured in the spring (March-June). Summer (July-October) concentrations were intermediate.

    b)  Winter composites were up to 3 times more mutagenic with added metabolic activation (+S9) than without (-S9) while activities of spring composites were not significantly changed by metabolic activation. This implies that both direct-acting (e.g., $NO_2$pyrene-like) and indirect-acting (e.g., BAP-like) mutagens are present in winter while in spring direct-acting mutagens predominate.

    c)  Annual average concentrations of mutagenicity and POM did not change significantly over the period between November 1979 and June 1982.

## II. EXPERIMENTAL APPROACH

This project was carried out in several concurrent and interconnected parts. One part was directed towards the refinement and standardization of chemical and microbiological methods for measuring selected carcinogens and mutagens in community air. A second part of the project consisted of three brief periods of intensive sampling and analysis to identify the sources of mutagenic actvity and POM in Contra Costa County community air. A third part was the continuation, on a limited basis of the community air mutagen-carcinogen monitoring in Contra Costa County, initiated in 1978 under a grant from the EPA. This chronic phase consisted of measuring particulate mutagens and carcinogens in seasonal composites collected at the permanent air monitoring stations in Richmond, Concord and Pittsburg.

### A. Intensive Sampling for Mutagen Source Identification

The central part of the study consists of three brief periods of intensive sampling and analysis designed to investigate the sources of mutagenic activity. The sampling and analytical plan for mutagen source identification is shown in Table 1.

Samples were collected at four locations (Richmond, Martinez, Concord and Pittsburg) in Contra Costa County. Three (Richmond, Concord and Pittsburg) are permanent stations of the Bay Area Air Quality Management District (BAAQMD). The BAAQMD stations are located so as to reflect the quality of community air breathed by northern Contra Costa residents. The fourth site, a temporary location at the Mountain View Sanitary District, Martinez, is specifically located to sample industrial emissions. All four are located in the industrialized portion of the county (Figure 1). The characteristics of each site were as follows:

Concord    -    Near the intersection of two major streets with a combined daily traffic count of approximately fifty thousand. Site is in a residential and commercial area.

TABLE 1

SAMPLING AND ANALYTICAL PLAN FOR MUTAGEN SOURCE IDENTIFICATION

**Day-Night Collection:**   6 a.m. - 6 p.m.
                              6 p.m. - 6 a.m.

**Collect Particulates on:**

| Hi-vol #1 (glass fiber) | Analytical Method | Agency Performing Analysis |
|---|---|---|
| Mass | Gravimetric | AIHL |
| Sulfate | Turbidimetric | AIHL |
| Nitrate | Colorimetric | AIHL |
| Lead | X-ray Fluorescence | AIHL |
| Organics | Benzene Extraction | AIHL |

Hi-vol #2 (glass fiber)
   Refrigerate immediately

| | | |
|---|---|---|
| Mutagenicity | Ames | AIHL |
| PAH | HPLC | AIHL |

Dichotomous Samplers
   (membrane or Teflon filter)

| | | |
|---|---|---|
| Multielemental analysis | Energy Dispersive X-ray Fluorescence | DHS-LBL |

**Collect Gas Data**

| | | |
|---|---|---|
| $NO_x$ | Chemiluminescence Photometry | BAAQMD |
| CO | Non-Dispersive Infra-red Absorption | BAAQMD |
| $SO_2$ | Fluorescence Photometry | BAAQMD |
| $O_3$ | Ultraviolet Absoprtion | BAAQMD |

**Collect Meteorological Data**

| | | |
|---|---|---|
| Wind direction Wind speed | | BAAQMD |
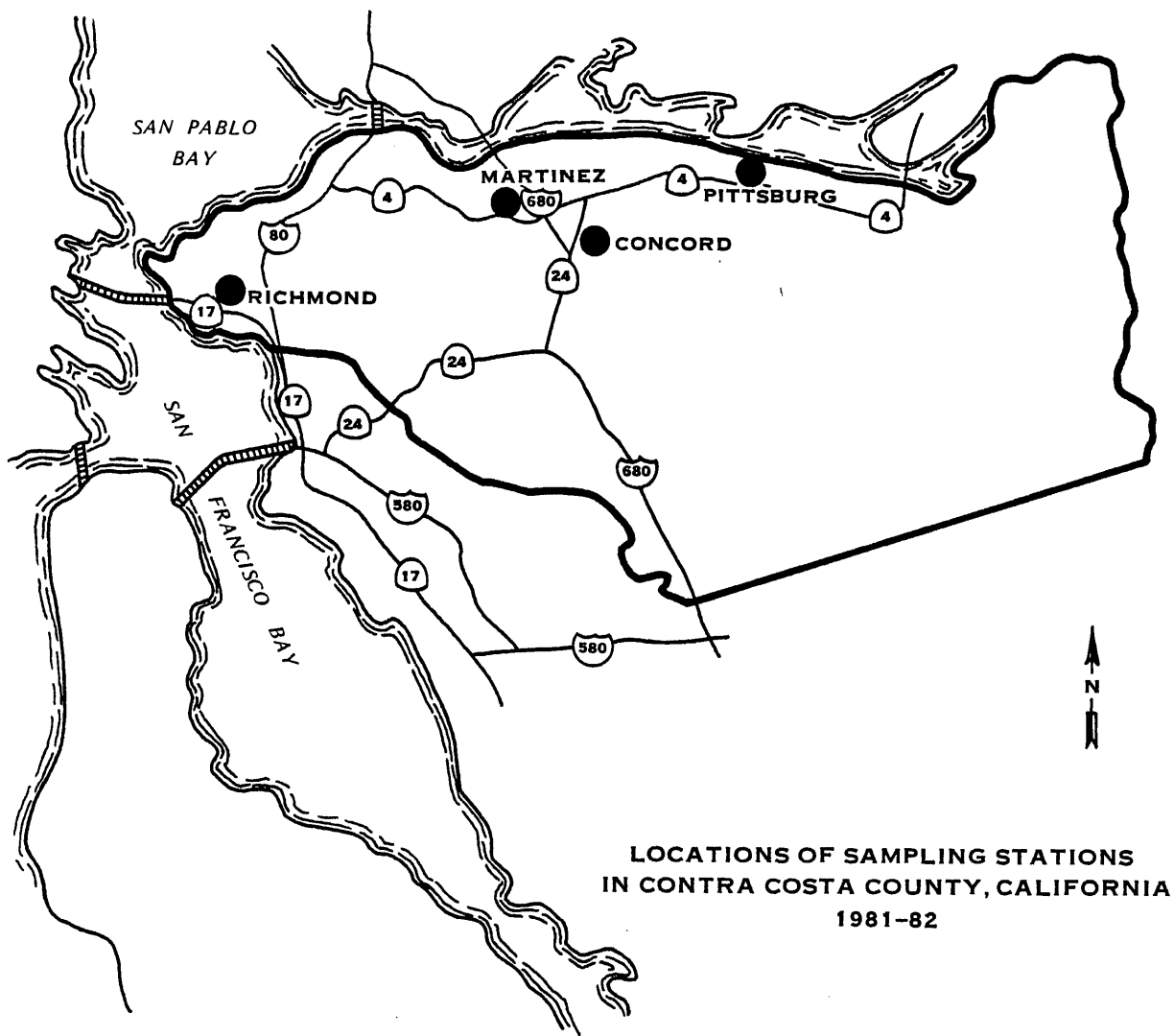
LOCATIONS OF SAMPLING STATIONS
IN CONTRA COSTA COUNTY, CALIFORNIA
1981–82

FIGURE 1

Richmond     —     Close to a major city street with a daily traffic count of thirty thousand. Industry is located 1 to 2 miles west of the site.

Pittsburg    —     Forty feet from a roadway with a daily traffic count of ten thousand. An oil burning electrical power plant is also located one half mile north of the site.

Martinez     —     Petroleum refinery located about 1000 feet west of the site, which is also approximately 400 feet east of a freeway where the daily traffic counts is sixty thousand. Residential tracts are nearby.

Each location had two hi-vol samplers and one dichotomous sampler to collect particulates for chemical and mutagenic analysis. Gaseous pollutant concentrations (CO, $SO_2$, NO, $NO_2$ and $O_3$) were also measured. These and other variables are defined in Table 2. Three 36 hour sampling episodes were selected, one in the winter, another in the summer, and the third in the fall when meteorological conditions for source reconciliation were favorable. Desirable "typical" conditions for the seasonal episodes were as follows:

Summer:   Westerly flow, inversion height 200-500 m. Sample during the occurrence of high oxidant days in July through August.

Fall:     Stagnant air mass, light and variable winds, inversion height 0-200 m. During the September and October period there frequently are concurrent high concentrations of all the gaseous and particulate pollutants.

Winter:   Air drainage from the east, 0-200 m inversion height. Typically high TSP and $NO_2$ days in November through January.

The summer sampling episode was carried out August 6-7, 1981, the fall episode October 20-22, 1981 and the winter episode January 13-15, 1982.

TABLE 2

ACRONYMS FOR VARIABLES USED IN THE
ANALYSIS AND INTERPRETATION OF CONTRA COSTA DATA

| TSP | Total Suspended (Hi-vol) Filter Mass | $\mu G/M^3$ |
|---|---|---|
| FDCX | Dichotomous Fine ($<$ 2.5 $\mu$m) Mass | $\mu G/M^3$ |
| CDCX | Dichotomous Coarse (2.5-15 $\mu$m) Mass | $\mu G/M^3$ |
| IP | FDCX + CDCX | $\mu G/M^3$ |
| IP/TSP | [FDCX + CDCX]/TSP | --- |
| $SO_4$ | Sulfate (Hi-vol) Mass | $\mu G/M^3$ |
| $NO_3$ | Nitrate (Hi-vol) Mass | $\mu G/M^3$ |
| BSO | Benzene soluble Organics (Hi-vol) | $\mu G/M^3$ |
| CHR | Chrysene | $NG/M^3$ |
| BAP | Benzo(a)pyrene | $NG/M^3$ |
| COR | Coronene | $NG/M^3$ |
| BO | Benzanthrone Isomers | $NG/M^3$ |
| BAA | Benz(a)anthracene | $NG/M^3$ |
| BBF+ BEP | Benzo(b)fluoranthene | $NG/M^3$ |
| BKF | Benzo(k)fluoranthene | $NG/M^3$ |
| DBA | Dibenz(ah)anthracene | $NG/M^3$ |
| BGP | Benzo(ghi)perylene | $NG/M^3$ |
| PAH | Sum Unsubstituted PAH + BO | $NG/M^3$ |
| IRON | Iron Fine + Iron Coarse | $NG/M^3$ |
| NICKEL | Nickel Fine + Nickle Coarse | $NG/M^3$ |
| ZINC | Zinc Fine + Zinc Coarse | $NG/M^3$ |
| BROM | Bromine Fine + Bromine Coarse | $NG/M^3$ |
| DC LEAD | Lead Fine + Lead Coarse | $NG/M^3$ |
| BR/PB | Dichot Bromine/Dichot Lead | --- |

| M398PS9 | Revertants per $M^3$ in TA98 + S9 | $REV/M^3$ |
|---|---|---|
| M398MS9 | Revertants per $M^3$ in TA98 - S9 | $REV/M^3$ |
| M398NRM | Revertants per $M^3$ in TA98NR - S9 | $REV/M^3$ |
| NR/98M3 | M398NRM/M398MS9 | --- |
| BSO98PS9 | Revertants per BSO in TA98 + S9 | $REV/\mu G$ |
| BSO98MS9 | Revertants per BSO in TA98 - S9 | $REV/\mu G$ |
| BSO98NRM | Revertants per BSO in TA98NR - S9 | $REV/\mu G$ |
| NR/98BSO | BSO98NRM/BSO98MS9 | --- |

| $O_3$ | Ozone | PPHM |
|---|---|---|
| CO | Carbon Monoxide | PPM |
| $NO_2$ | Nitrogen Dioxide | PPHM |
| NO | Nitrogen Oxide | PPHM |
| $SO_2$ | Sulfur Dioxide | PPHM |

During each of the 36 hour sampling episodes, separate day and night samples were collected (6 a.m. to 6 p.m.; 6 p.m. to 6 a.m.).

B.    Collection and Analysis of Seasonal Composites

The experimental approach and logistical plan used in the chronic phase is similar to that used previously (16, 17) but incorporates improvements in sample collection and analytical techniques (Figure 2). Samples were collected at the three permanent stations of the BAAQMD network (Concord, Pittsburg and Richmond) used for intensive sampling. BAAQMD personnel service these stations regularly, so the cost of sample collection was minimal. Hi-vol filter samples were collected every sixth day at each station for routine monitoring purposes and were analyzed for TSP, $SO_4^=$, and $NO_3^-$ by the BAAQMD and for BSO and PB by AIHL. A portion of each filter was composited for PAH and mutagenicity testing. Filters from each of the three stations were composited over four-month intervals (July-October, November-February, March-June), to give composite samples for analysis. These periods approximate the three meteorological seasons in the San Francisco Bay air basin and also correspond with those used in the previous study in Contra Costa County, November 1978 - October 1979 (16, 17).

In the current project samples collected during the period November 1979-June 1982 were composited for analysis of PAH and mutagenic activity. Analysis of these samples provides a continuous data base of the concentrations of specific PAH and mutagenic activity found in Contra Costa air particulate material collected over a 32 month period. Results of PAH and mutagenicity measurements in composite samples were compared with TSP, $NO_3^-$, $SO_4^=$, PB and BSO results on a season-by-season basis. The PAH and mutagenicity levels were compared with those previously measured and the results were also made available to the State's Resource for Cancer Epidemiology.

III.  EXPERIMENTAL METHODS

The detailed methods used to collect and analyze pollutant gases and particulate material and procedures for evaluation of results were modified from previous

FIGURE 2 Logistical Plan for Analysis of Hi-Volume Air Filters Collected in Contra Costa County, November 1, 1978 - October 31, 1979

**FILTERS**
1. Collected
2. Weighed
3. Delivered to AIHL (BAAQMD)

**FILTERS**
1. Logged in
2. Deposit area measured
3. Cut and distributed for analysis (AIHL)

**TSP Gravimetrically (BAAQMD)**

1/2

1/4

**Analyzed for BSO by soxhlet extraction (AIHL)**

**Analyzed for MUTAGENIC ACTIVITY in the Ames Assay (AIHL)**

(Supple ment)

To BAAQMD

**Analyzed for NO$_3^-$, Colorimetrically SO$_4^=$, Turbidimetrically (BAAQMD)**

**Analyzed for PAHs by GC-MS, HPLC (AIHL)**

**Analyzed for Pb by X-ray fluorescence (AIHL)**

**DATA BANK (AIHL)**
1. Results recorded
2. Data key punched and entered into computer
3. Cumulative results printed out each 4 months

studies (17). Briefly, the current status of methods and procedures used is as follows:

A.  Sampling of Air Particulates and Gases

Air particulate material for mutagenic and PAH testing was collected on 8" x 10" glass fiber filters (S & S) in standard hi-vol samplers. The sampling rate was 55-60 $m^3$ per hour.

Size-selective particulate samples for multielement analysis were collected on 37 mm Teflon Fluoropore (0.2 micron) filters (Ghia) in standard dichotomous samplers (Anderson and Sierra Models). Sampling was at a rate of 1 $m^3$ per hour.

Gases were sampled using specific monitors described below.

B.  Chemical Analysis of Trace Elements and Standard Air Pollutants

Measurement of trace elements (Pb, Br, Zn, Fe, Ni) on particulate samples collected with dichotomous aerosol samplers was done by x-ray fluorescence analysis under contract with R. Giaque, Lawrence Berkeley Laboratory (30).

Analyses of the standard chemical pollutants measured in the ARB air quality network were carried out by the BAAQMD and AIHL using the standard methods. TSP is determined gravimetrically, Pb by energy dispersive x-ray fluorescence, $SO_4^=$ turbidimetrically, by SulfaVer, $NO_3^-$ by a colorimetric procedure utilizing NitraVer 6 and NitraVer 3 pillows, and BSO by benzene extraction followed by gravimetric determination.

Gaseous pollutants were measured using specific gas monitors; $O_3$ was measured by ultraviolet absorption with a Dasibi Ozone Monitor Model 1003-AH; CO was measured by infrared absorption with a Bendix Analyzer Model 8301-5CA; NO and $NO_2$ were measured by chemiluminescence with a Thermal-electron Model 14D analyzer; $SO_2$ was measured by fluorescence using a Thermal-electron Model 43 pulse-fluorescence analyzer. All methods are EPA reference or equivalent to the EPA reference methods.

C.   Analysis of Particulate Polycyclic Aromatic Hydrocarbons (PAH)

As in our previous work (17), one quarter to one half of a hi-vol filter was cut into small, ca. 1 cm$^2$ pieces, and extracted in 200 mL trisolvent (toluene:methylene chloride:methanol(1:1)) (MCB, Omni-Solv) for 1 hour at 45°C in an ultrasonic bath. The extract was filtered through a 0.5 um fluoropore membrane, the filter rinsed with 100 mL trisolvent, and the two extracts combined. The 300 mL extract was concentrated ca. 20 fold on a rotary evaporator at 45-50°C, then transferred to a heat block at 45°C and the remaining 5 mL solvent removed under a stream of nitrogen. The residue was redissolved in a small volume (<0.2 mL) acetonitrile and 10 uL of the concentrated extracts analyzed by HPLC. Previously (17) clean-up of extracts was carried out to separate PAH from interfering material. Further experiments have demonstrated that the direct injection of trisolvent extracts into the HPLC without clean-up gives equivalent results in less time.

Separation of PAH was performed on an ultrasphere ODS 4.6 x 2.50 mm analytical column. Column eluant was monitored using ultraviolet absorption (at 300 and 400 nm) and fluorescence emission (excitation 295 nm; emission 398 nm). The on-line fluorescence measurements were made with a Perkin-Elmer Model MPF-44A spectrofluorometer. Ultraviolet absorption was monitored with a Varian Vari-Chrom UV-Vis detector. Extracts were chromatographed using a linear gradient from 70% acetonitrile in water to 100% acetronitrile in 50 minutes. The flow rate was 0.8 mL/min, the temperature 30°C and the chart speed 1 cm/min. Sample injection was made with a sample loop operated by a rotary valve using a 10 uL injection volume.

The efficiency of extraction of PAH from hi-vol filters has been investigated. Fluorescence measurements show that at least 94% of unsubstituted PAH containing four to seven rings (chrysene to coronene) were recovered from spiked filters using the procedure described. Greater than 98% of the oxy-PAH, benzanthrone is removed from spiked filters with a single 1 hour extraction. For simultaneous extraction of both polar (e.g., benzanthrone)

and nonpolar compounds (e.g., coronene), trisolvent proved to be more efficient than either cyclohexane or dichloromethane.

Sample chromatograms and chromatographic conditions used for separation of a standard calibration mixture of unsubstituted PAH and benzanthrone are illustrated in Figure 3 and Figure 4 respectively. The corresponding chromatograms of air particulate extracts analyzed for unsubstituted PAH and benzathrone are shown in Figures 5 and 6 respectively. Peaks observed in the air extract chromatograms were identified by several means. Initial identifications were made using retention times. Confirmations were achieved by stop-flow spectrofluorometric comparisons (Figures 7 and 8). Excitation and emission characteristics of PAH in a standard mixture and in an aerosol extract are shown in Table 3. In the case of benzanthrone, the mass spectrum of individual mass fragments was compared with a reference standard (Figure 9). The chromatographic and spectral characteristics used to identify benzanthrone (including all isomers) in air particle extracts are summarized in Table 4. Quantitative analysis was routinely performed by comparing the corresponding peak heights in air sample with those in a standard reference mixture of compounds. The Standard Compounds used in this study were from the following suppliers: 7-H-benz(de)anthracene-7-one(BO) from BASF Aktiengesellschaft, City, Germany. Chrysene (CHRY), benz(a)anthracene (BAA), benzo(b)fluoranthene (BBF), benzo(e)pyrene (BEP), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), dibenz(a,h)anthracene (DBA), benzo(ghi)perylene (BGP) and coronene (COR) from Nanogens, City, California. The structures of these molecules are shown in Figure 10.

D.  Synthesis and Characterzation of Nitroarenes

Oxides of nitrogen (e.g., $NO_2$) plus a trace of $HNO_3$ can react with unsubstituted PAH in diesel exhausts, on filters and possibly also in air to form nitro-substituted PAH (25-27). Such compounds include both direct-acting and indirect-acting mutagens in the Ames test and some nitr PAH (e.g. dinitropyrenes) are highly mutagenic, orders of magnitude more active than the parent PAH (20,29). Several nitro PAH including isomers of nitropyrene, nitrofluoranthene and nitroacenaphthene have been detected in

CONDITIONS

Column:  250x4.6mm
         Ultrasphere ODS

Flow:    0.8 ml/min.
         60/40 ACN/H₂O to
         100% ACN in 50 min.

Detection:  UV at 300nm, 0.05 aufs -----
            Relative Fluorescence
            at 295/398nm ———

1 CHRY (10ng)
2 BAA (10ng)
3 BBF+BEP (15ng+15ng)
4 BKF (5ng)
5 BAP (10ng)
6 DBA (2.5ng)
7 B(GHI)P (20ng)
8 CORONENE (50ng)
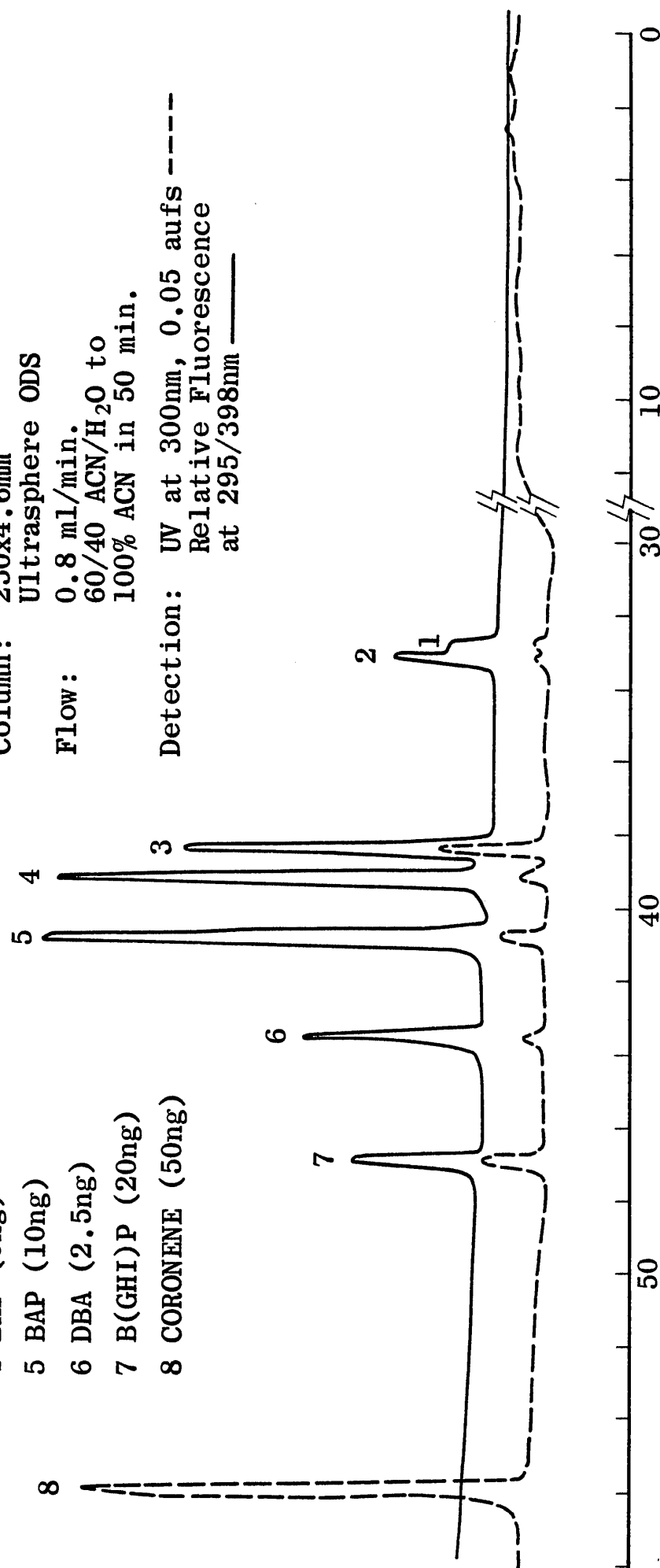
Time (min.)

FIGURE 3. HPLC of the PAHs in a Standard Mixture

-28a-

CONDITIONS
Column: 250 x 4.6mm
         Ultrasphere ODS

Flow:   0.8 ml/min
        60/40 ACN/$H_2O$ to
        100% ACN in 50 min.

Detection: UV at 400 nm 0.02 aufs ----
           Relative Fluorescence
           at 407/460 nm ————

7-H-benz(d,e)anthracen-7-one
(24ng)

Time (min.)
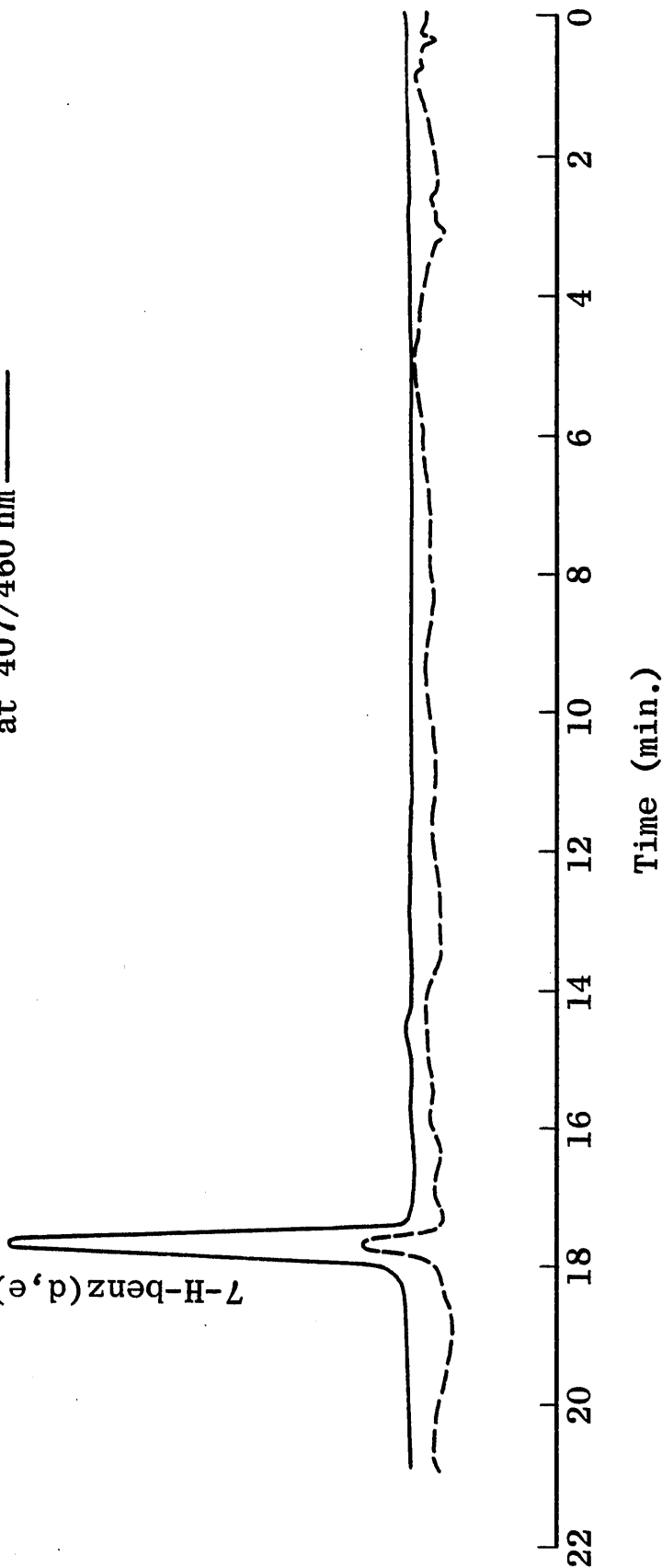
FIGURE 4. HPLC of 7-H-benz(d,e)anthracen-7-one Standard.

CHROMATOGRAPHIC
CONDITIONS SAME
AS IN FIGURE 3

1 CHRY
2 BAA
3 BBF + BEP
4 BKF
5 BAP
6 DBA
7 B(GHI)P
8 CORONENE

Time (min.)
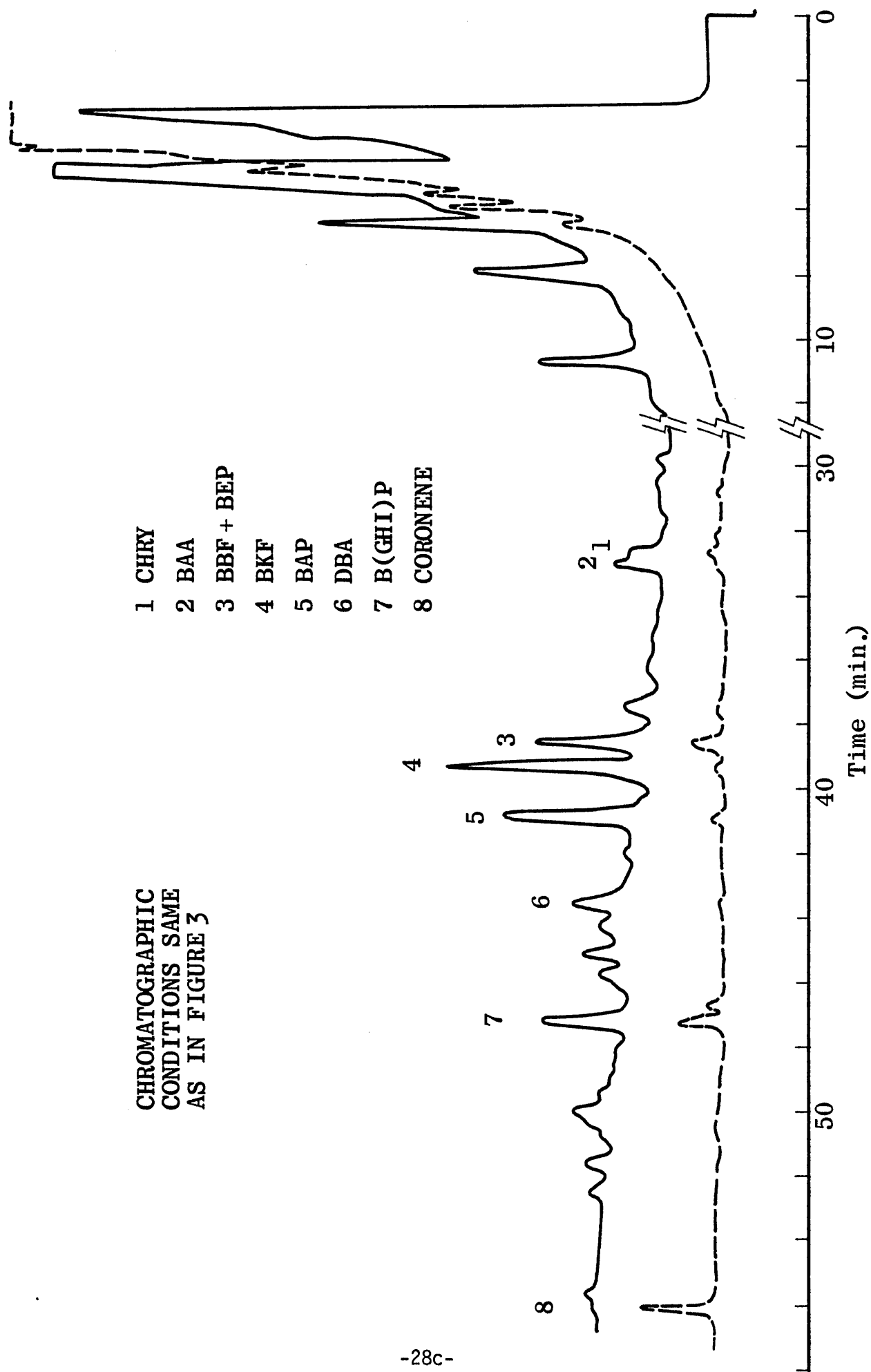
FIGURE 5. HPLC of PAHs Extracted from a Glass Fiber Filter   Martinez, CA., October 21, 1981.

-28c-

CHROMATOGRAPHIC
CONDITIONS SAME
AS IN FIGURE 4

7-H-benz(d,e)anthracen-7-one

Time (min.)
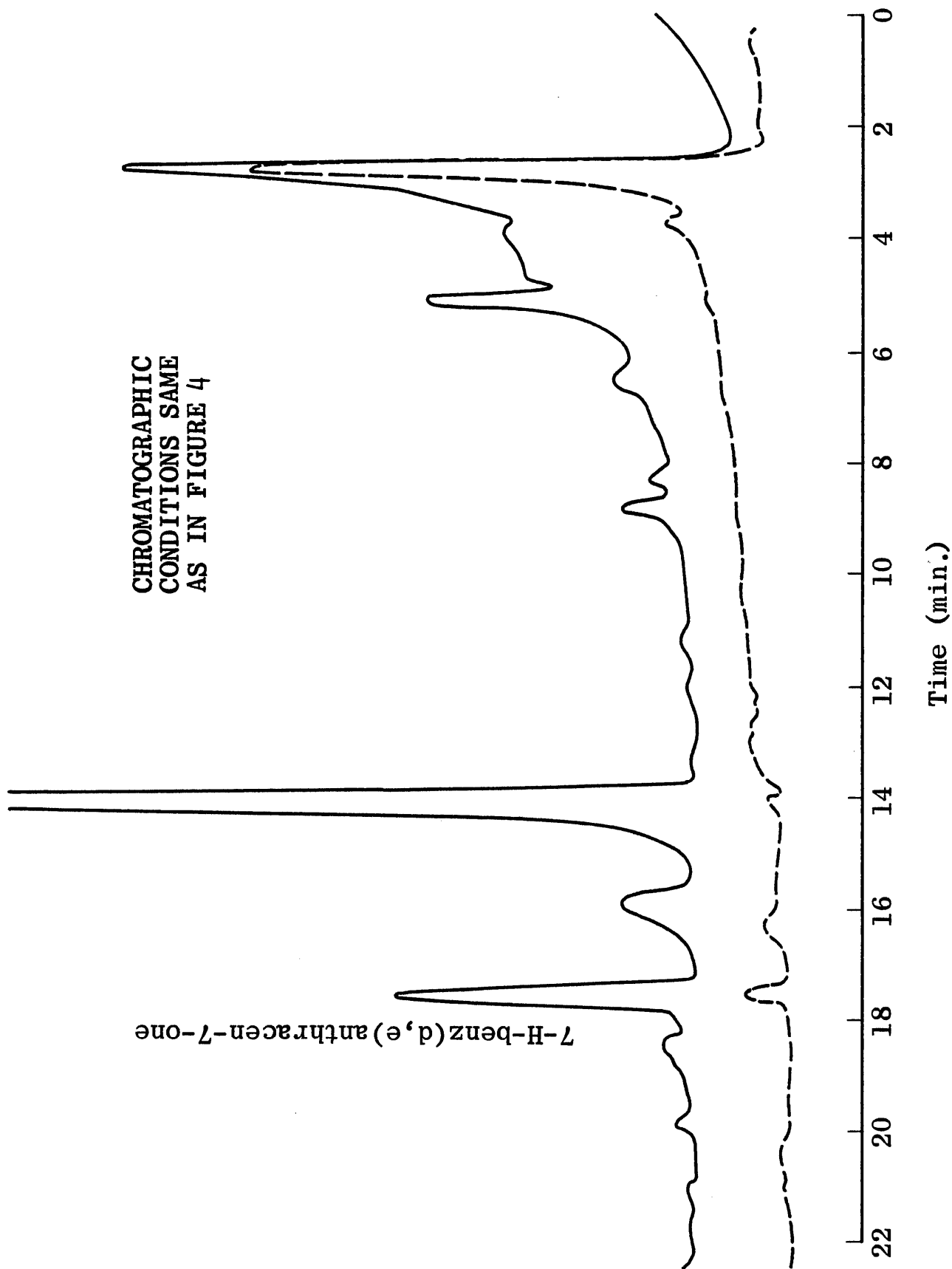
FIGURE 6. HPLC of 7-H-benz(d,e)anthracen-7-one Extracted from
a Glass Fiber Filter   Martinez, CA., October 21, 1981.
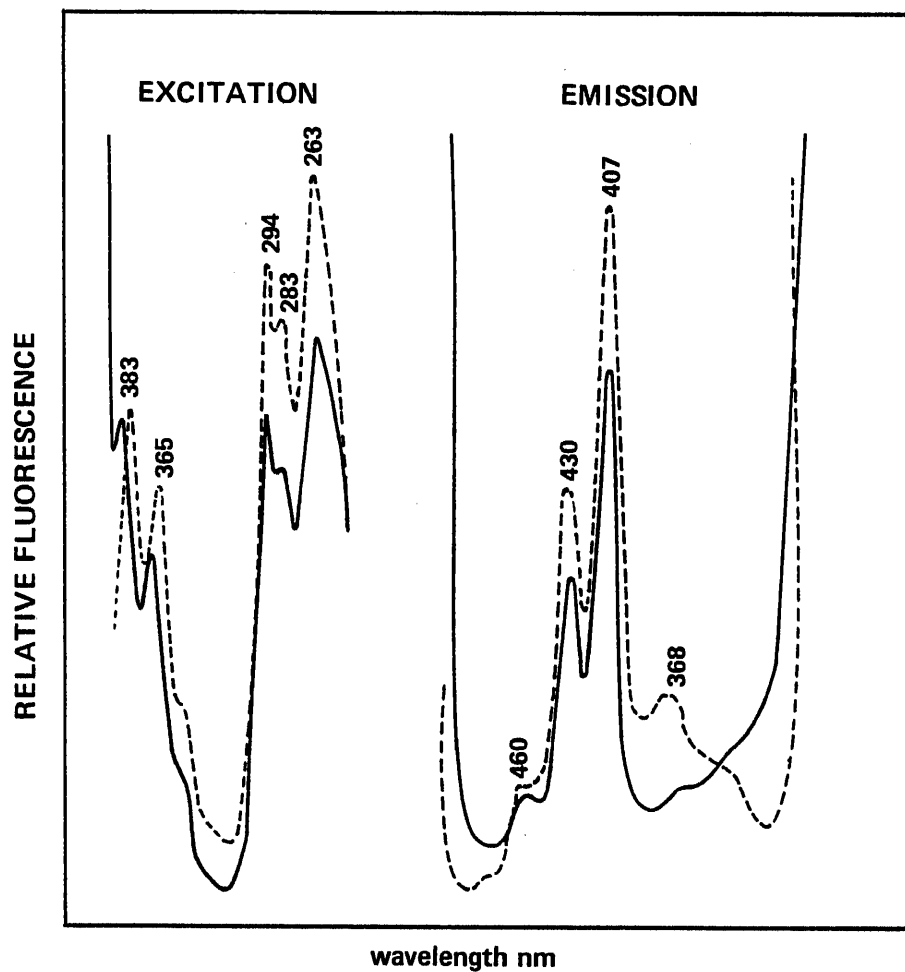
Figure 7. Excitation and emission spectra obtained by a stopped-flow scanning during HPLC analysis.

-------- Peak No. 5 in Figure 5　　————— BAP Standard
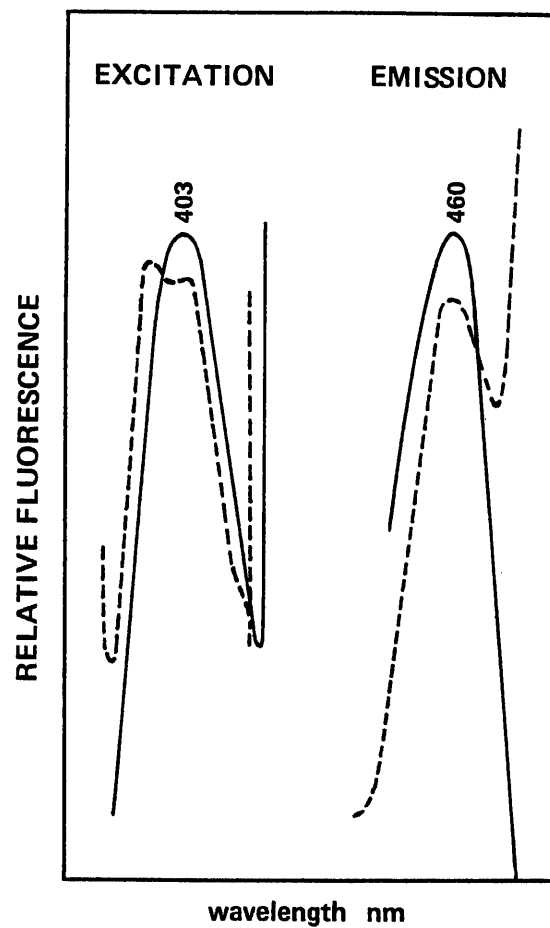
Figure 8. Excitation and emission spectra
obtained by a stopped-flow scanning
during HPLC analysis.

------ The peak in Figure 6

———— 7-H-benz(d,e)anthracen-7-one
standard

TABLE 3

COMPARISON OF FLUORESCENT SPECTROSCOPIC CHARACTERISTICS
OF PAH IN AIR PARTICLES AND IN A STANDARD MIXTURE

| Compound | Wavelength Excitation Maxima (nm) | | Wavelength Emission Maxima (nm) | |
|---|---|---|---|---|
| | Sample | Standard | Sample | Standard |
| Chrysene | 265 | 265 | 365,384,404 | 365,384,404 |
| Benz(a)anthracene | 287 | 283 | 390,411,434 | 390,411,435 |
| Benz(b)fluoranthene + Benz(e)pyrene | 290 | 297 | 440 | 440 |
| Benz(k)fluoranthene | 306,381,402 | 304,378,400 | 413,436 | 413,434 |
| Benz(a)pyrene | 263,295 | 263,294,365 | 408,430 | 407,430,460 |
| Dibenz(ah)anthracene | 288 | 295 | 382,398,420 | 398 |
| Benz(ghi)perylene | 297,363,381 | 297,362,381 | 411,420,430 | 410,420,430 |
| Coronene | 301,340 | 337 | 430,450 | 450 |
| Benzanthrone | 399,417 | 399 | 466 | 466 |
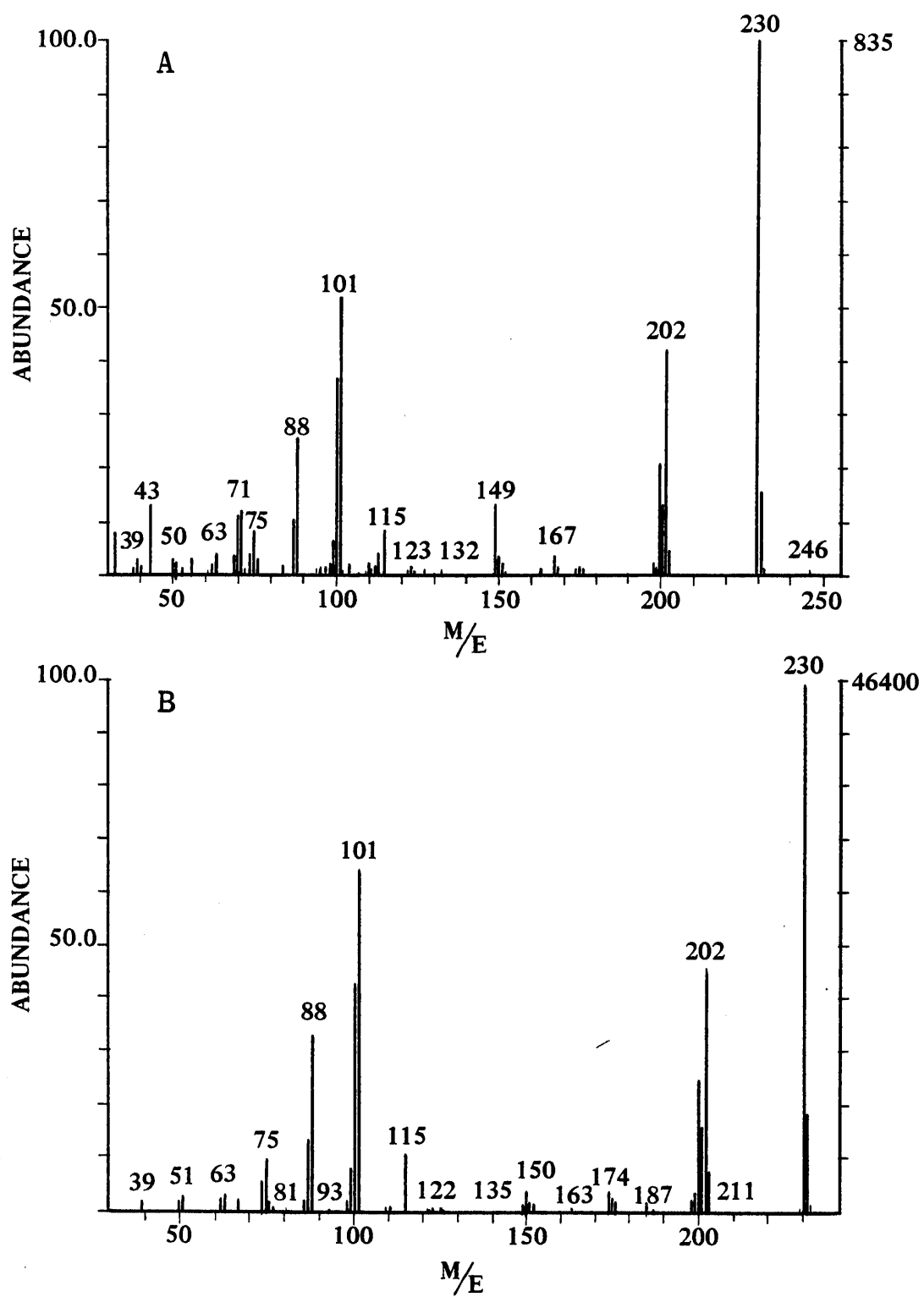
FIGURE 9. (A) EI mass spectrum of eluant from HPLC, identified as
7-H-Benz(de)anthracene-7-one, (B) EI mass spectrum of
7-H-Benz(de)anthracene-7-one standard.

## TABLE 4

### CHROMATOGRAPHIC AND SPECTRAL CHARACTERISTICS OF 7-H-BENZ(D,E)ANTHRACEN-7-ONE

| | Sample | Standard |
|---|---|---|
| **HPLC** | | |
| Retention time (min.) | 17.7 | 17.7 |
| **Fluorescence, $\lambda$ max** | | |
| excitation | 403 418 | 403 |
| emission | 460 | 460 |
| **EI Mass Spectrum (70 e.v.)** | | |
| M/Z (relative intensity) | 230(100) 202(42) 101(52) 88(27) | 230(100) 202(46) 101(64) 88(33) |
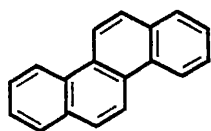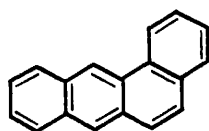
Chrysene     Benz(a)anthracene     Benzo(e)pyrene
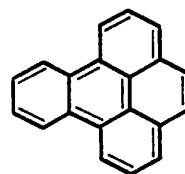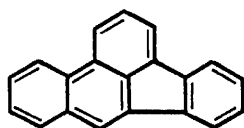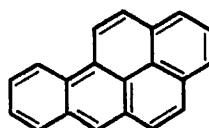
Benzo(b)fluoranthene     Benzo(a)pyrene     Benzo(k)fluoranthene
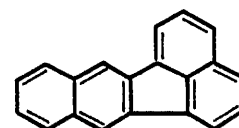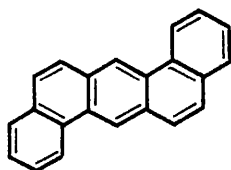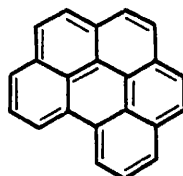
Dibenz(a,h)anthracene     Benzo(ghi)perylene     Coronene
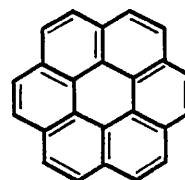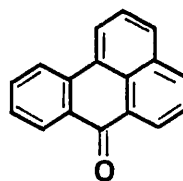
7-H-benz(d,e)anthracen-7-one

FIGURE 10. STRUCTURE AND NOMENCLATURE OF 10 POM's

diesel exhaust (20) and evidence for nitro-aromatics in community air particulates has been presented (21,22,27).

We are attempting to detect chemical nitro PAH in air particulate material by reducing the nitro compounds to the corresponding amino PAH (31). The latter are highly fluorescent molecules which may be detectable in ambient air samples even at very low concentrations. Procedures for reduction of air filter extracts have been developed. Reduction and analysis of reduced air filter extracts by HPLC reveal the presence of several strongly fluorescent materials not present in unreduced samples.

Critical to the success of this approach is the availability of $NO_2PAH$ standards. Such standards are not readily available so considerable effort has been expended to synthesize and isolate $NO_2PAH$ of special interest. We have initially focused on preparation of derivatives of PAH found in relatively high concentrations in air samples. To date, twenty nitro PAH standards have been prepared. These include isomers of nitrocoronene, nitrobenzo(ghi)perylene, nitrobenzo(k)fluoranthene, nitrophenanthrene, nitrobenz(e)pyrene, nitrotriphenylene and nitrodiben(a,c)anthracene. The specific isomers of some compounds have been identified and the mutagenicities of these compounds are still being determined.

The Appendix describes in detail progress in the synthesis and mutagenic characterization of highly mutagenic nitrocoronene and nitrobenz(g,h,i) perylene derivatives. Briefly, synthesis of $NO_2PAH$ was performed by adding nitronium tetrafluoroborate dissolved in anhydrous acetonitrile to solutions of PAH. Purification was achieved by adsorbtion of the nitro derivatives to silica gel, washing with n-hexane, desorbtion with dichloromethane, and fractionation by preparative high performance liquid chromatography. Identification of collected peaks was accomplished using electron impact mass spectrometry and high resolution proton magnetic resonance spectroscopy. Quantitation was done spectrophotometrically in acetonitrile using the absorption values from the major Soret bands. Mutagenic testing was performed in strain TA98, several of its nitroreductase-deficient derivatives (29) and TA97 (32).

Unusually high mutagenicities of nitro derivatives of benzo(ghi)perylene (BGP) and coronene (COR) were observed. BGP and COR are major constituents of PAH found in automobile exhaust. Nitration of these PAH by $NO_2$ and traces of $HNO_3$, during gasoline combustion therefore seems highly probable. $NO_2$PAH analysis of air particle extracts is in progress.

E.    Mutagen Testing Methods

Standard methods for extracting and compositing air particulate material from hi-vol glass fiber filters for mutagenicity testing of samples were as previously described (17). The solvent, a 1:1:1 mixture of methanol/dichloromethane/toluene (MCB, OmniSolv), (trisolvent) was prepared fresh daily and saturated with nitrogen ($N_2$). Extractions with trisolvent were carried out under reduced light, in an ultrasonic bath. Filters are cut and the pieces extracted for 20 minutes at maximum power in the ultrasonic bath containing water at $45^{\circ}C$. Extracts were filtered through 0.5 um fluoropore filters (Millipore); the air filter disks were re-extracted using fresh solvent and the filtrates combined. Previous comparisons have demonstrated that trisolvent extracts are more mutagenic than dichloromethane (DCM) extracts.

Compositing for mutagenic testing is performed by combining filter disks and extracting. Composite extracts were saturated with $N_2$ and the solvent volume reduced under vacuum at a temperature of $45^{\circ}C$ in a rotary evaporator. Composite samples, reduced twenty-fold in volume, are transferred to pre-weighed tubes placed in a heat block at $45^{\circ}C$ and the remaining extraction solvent removed under a stream of nitrogen. After weighing, residues are redissolved in dimethyl sulfoxide (DMSO) for mutagenic analysis.

Standard Ames Test

The standard plate incorporation method for detecting mutagens with the Salmonella/mammalian microsome test was used as described by Ames, et al. (8) with the following changes: rat liver homogenate (S9) is obtained from commercial sources or prepared from rats fed commercial rodent foods and anesthesized with carbon dioxide prior to surgery. Plates were incubated

for 60-70 instead of 48 hours. S9 protein concentrations are determined by the method of Lowry et al. (33).

Negative solvent and S9 sterility controls and positive controls for each strain used were performed with each experiment. The control mutagens used were 2-nitrofluorene, 4-nitroquinoline oxide, quercetin and 2-amino-fluorene. The coefficient of variation among positive control values from experiment to experiment was approximately 25 percent.

Analysis of previous air samples has shown that TA98 is the most sensitive strain. Therefore, extracts were analyzed in TA98, and in the isogenic nitroreductase mutant TA98NR. Determinations were made with and without added rat liver S9 at 0.6 mg protein per plate. Duplicate determinations were made at several doses when sufficient sample was available. The results were expressed as revertants per $m^3$ or revertants per ug organic extractable mass.

## Microsuspension Assay

A modification of the Salmonella liquid incubation assay was found to increase the sensitivity for complex mixtures (34). This modified Ames test protocol was used to determine mutagenic activity of airborne particulate matter. Composite hi-vol extracts of Berkeley air particles were approximately 10 times more mutagenic (in units of revertants/$m^3$) in the modified "microsuspension" assay than in the plate incorporation test using strain TA98 $\pm$ S9 (Figure 11). The modification was also at least 10 times more sensitive for a variety of widely used control mutagens. To test the applicability of the microsuspension assay for air samples of limited sample size, we measured the mutagenic activity of "fine" (diameter $\leq 2.5$ um) particles collected with an automatic dichotomous sampler (LBL Model 1). The air particles were collected at 2 hour intervals for 24 hours in Berkeley. Solvent extracts were prepared by sonication of filters. Mutagenicity was detected in samples containing the particle extract from less than one cubic meter of air. There was a definite diurnal pattern of mutagenic activity, reported as TA98 revertants per cubic meter air (Figure 12).

FIGURE 11. Dose-Response Curves for Aerosol Extracts Obtained from Hi-Vol Samples Comparing the Microsuspension and Standard Plate Incorporation Ames Test.
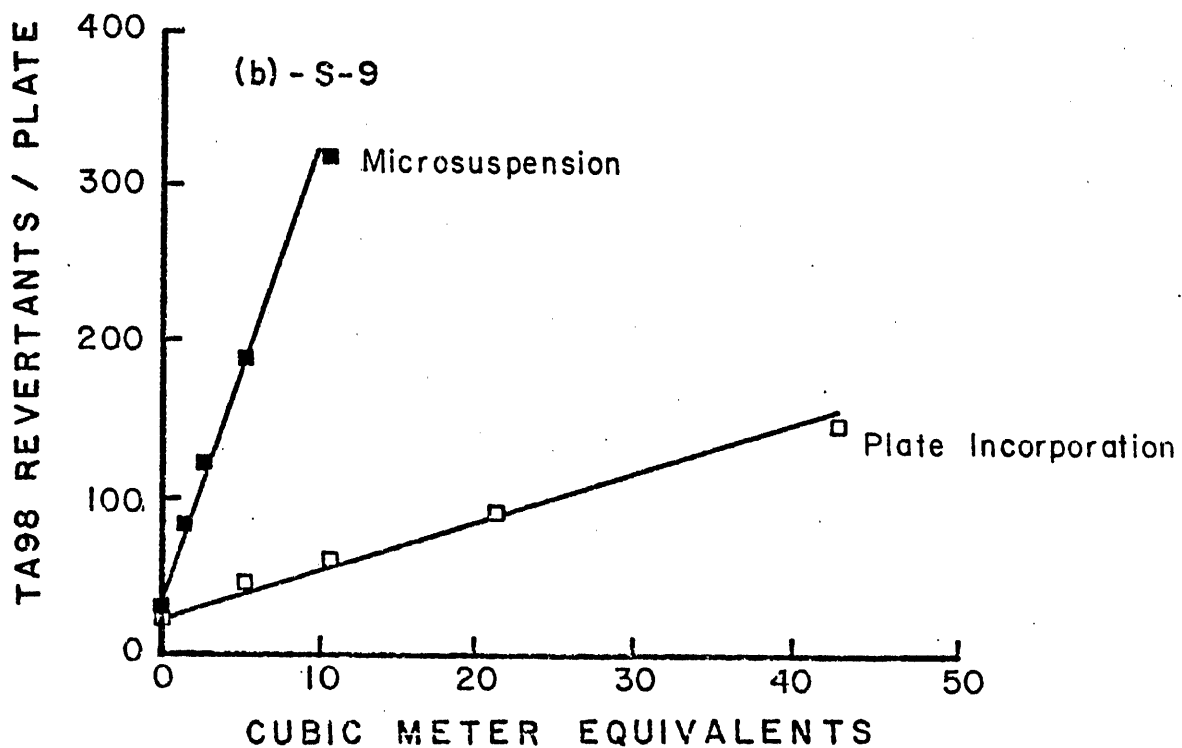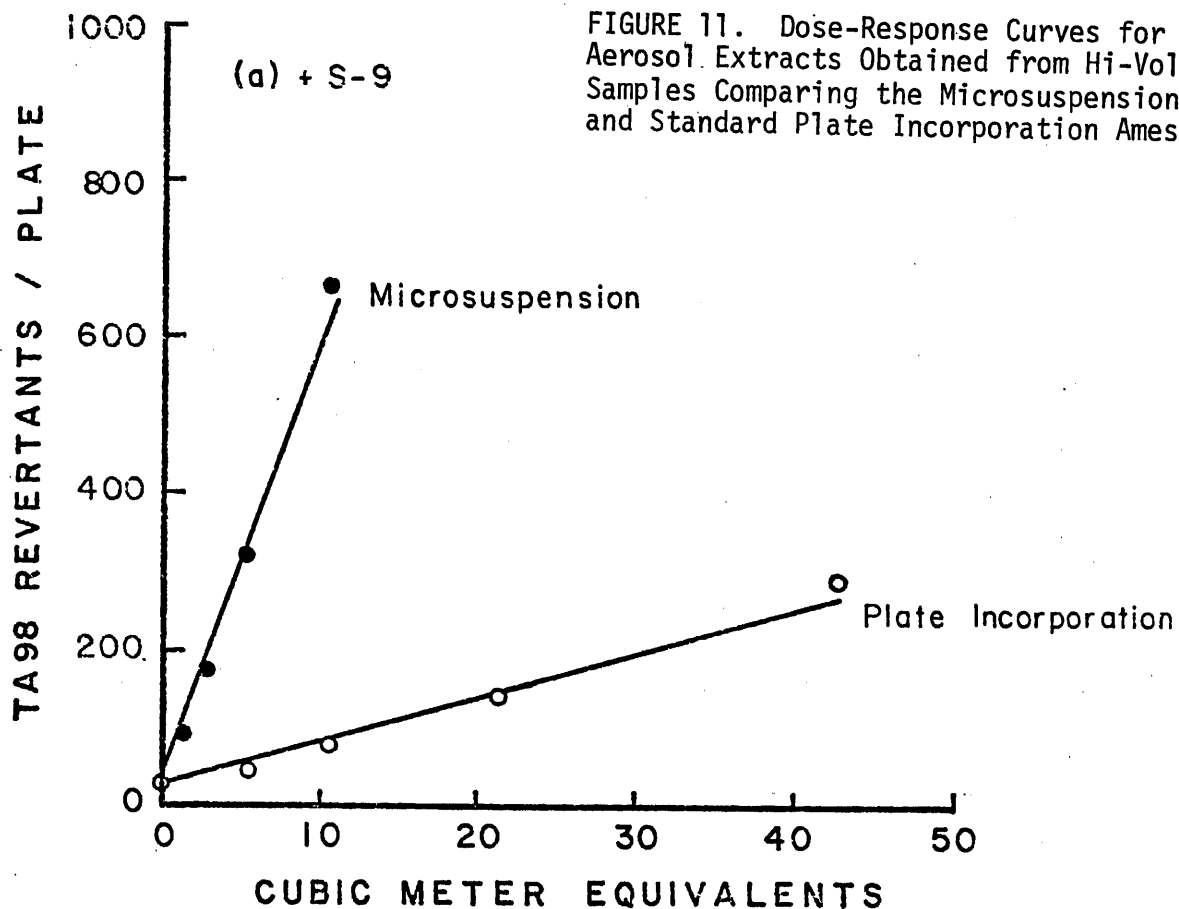
FIGURE 12

DIURNAL VARIATION

BERKELEY, FINE, TA98 +S9

Sample missing.

REVERTANTS/m³

TIME OF DAY (10/20/82)
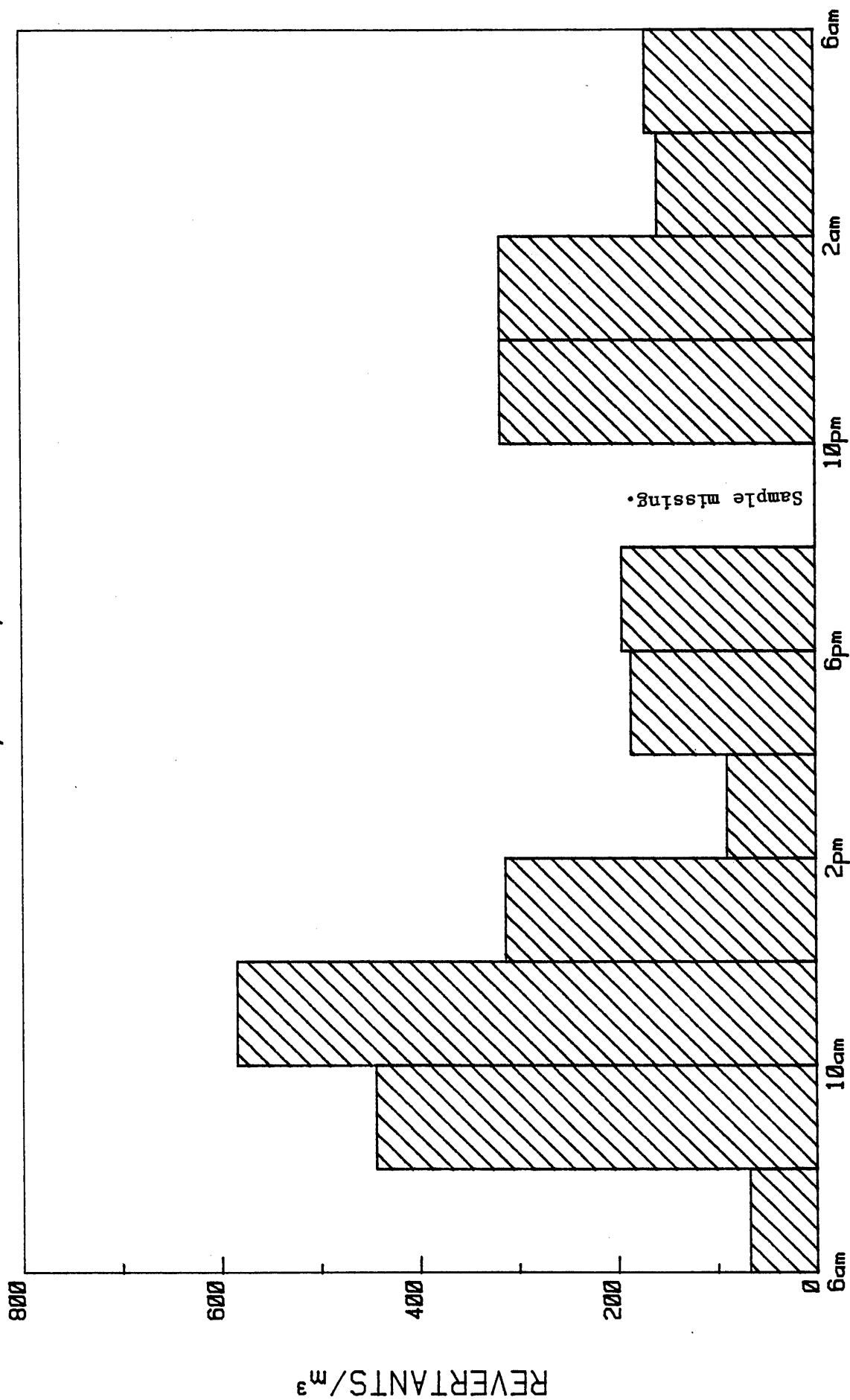
In future research the microsuspension modification will be especially useful in studies where sample size is a limiting factor. The increased sensitivity will allow diurnal pattern measurements, an important technique for assessing sources of mutagens.

F.  Statistical Techniques

Examples of the data bank, data decks and formats developed for this study are shown in Table 5-7. The data base contains results for the standard particulate air pollutants (TSP, lead, sulfate, nitrate and benzene soluble organics), polycyclic aromatic hydrocarbons (nine species), mutagenicity (in TA98 and TA98NR), five elements (iron, nickel, zinc, lead and bromine) on size-segregated aerosols, gaseous pollutants ($O_3$, $SO_2$, CO, NO, $NO_2$) and meteorological information. The statistical analysis is based on programs contained in the Statistical Analysis System (SAS). All programs were run on the CDC 6400 computer at the University of California, Berkeley. Simple correlation and multivariate analysis were performed.

Correlation analysis was done using Spearman rank order coefficients to compare mutagenicity variables with other potential predictor variables (e.g., Pb, $NO_3^-$, $SO_4^=$).

The basic strategy followed in the multivariate statistical analysis employs the results of the bacterial mutagenicity test as a response variable, and relates this information to a series of predictor variables (the various airborne chemical pollutants). If a consistent relationship arises between one or more of the predictor variables and the response variable, some insight may be gained as to mutagen source identification.

Following closely the description of Daisey and Kneip (35), factor analysis was used to identify principal types of emission sources and to select among pollutant source tracers. Factor analysis is based on the assumption that observed correlations between variables are due to some underlying structure in the data--source emissions and atmospheric. Processes including chemical and physical transformations, atmospheric transport and atmospheric dispersion. The complexity of the various emissions and atmospheric reactions

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# TABLE 5
# CONTRA COSTA INTENSIVE SAMPLING DATA BANK

STATION   EPISODE   START DATE   TIME   END DATE   TIME   1-30

MASS - ug/m3   ROOM TEMP HI-VOL - ug/m3

RTHV   CYCL   FDCX   CDCX   LEAD   SULFATE   NITRATE   ORGANICS   31-60

PAH ng/m3 [Frozen Hi-vol]

CHR   BAA   BBF + BEP   BKF   BAP   61-85

DBA   BGP   COR   BO + ISO   86-105

AMES rev/m3 [Frozen hi-vol]

TA 98 +S9   TA 98 -S9   TA 98NR +S9   TA 98NR -S9   106-125

DICHOT COARSE - ng/m3

IRON   NICKEL   ZINC   BROMINE   LEAD   126-155

DICHOT FINE - ng/m3

IRON   NICKEL   ZINC   BROMINE   LEAD   156-185

-32a-

TABLE 6

## HIVOL (INTENSIVE) DECK FORMAT

| Col. | Item |
|------|------|
| 1-4 | <u>Sample Type</u> |
| | RTHV - Room temp hi-vol |
| 5-9 | <u>Station</u> |
| | 07430 - Pittsburg |
| | 07433 - Richmond |
| | 07440 - Concord |
| | 07996 - Martinez |
| 10-15 | <u>Start Date</u> |
| | yr, mo, day |
| 16-19 | <u>Start Time</u> |
| 20-25 | <u>End Date</u> |
| 26-29 | <u>End Time</u> |
| 30-32 | <u>TSP</u> - ug/m$^3$ |
| | XXX |
| 33-36 | <u>Lead</u> - ug/m$^3$ |
| | X.XX |
| 37-40 | <u>Sulfate</u> - ug/m$^3$ |
| | XX.X |
| 41-44 | <u>Nitrate</u> - ug/m$^3$ |
| | XX.X |
| 45-48 | <u>Organics</u> - ug/m$^3$ |
| | XX.X |
| 49-52 | <u>Episode</u> |
| | I - period 1,2,3 |
| | II - period 1,2,3 |
| | III - period 1,2,3 |

TABLE 7

# HI-VOL INTENSIVE DECK

is shown pictorially in Figure 13 (adapted from reference 24). Source emissions and atmospheric reactions are the underlying "factors", "traits" or "dimensions" which determine the mutagenicity of air particle extracts. Factor loadings represent correlations between factors and variables. Geometrically, the factors may be considered as orthogonal axes in n-dimensional space (n = number of variables). The variables are points in that space and the coordinates of the points are the loadings of the variables on the factors. In the present study, Principle Axis factoring with Varimax rotation of the factors was employed.

Based on the results of the factor analysis, source tracers were chosen. Linear multiple regression models were developed in which mutagenicity and PAH (the response variables) were related to concentrations of source tracer pollutants (the predictor variables). These were of the form:

MUTA or PAH = $k_1C_1 + k_2C_2 + \ldots k_iC_i + R$

where MUTA = the mutagenicity of aerosol extracts;

PAH = the sum of the concentrations of the nine polycyclic aromatic species;

$C_i$ = The concentrations of source tracer pollutants

$k_i$ = The regression coefficients determined by least squares analysis;

R = The residual, i.e., the portion of MUTA or PAH not associated with the modeled sources.

The coefficients of the equation were determined by step-wise multiple regression in which the tracer pollutant accounting for the greatest proportion of the variation of MUTA or PAH is used to find a first order, linear regression equation of the form MUTA = $k_1C_1 + R_1$, where $R_1$ is the residual. The partial correlation coefficients (correlation after allowance for correlation with the first tracer) of the remaining tracer pollutants are then examined. The $C_i$ with the highest partial correlation coefficient with MUTA is selected next and a second regression equation of the form MUTA = $k_1C_1 + k_2C_2 + R_2$ is fitted. This process continues until all $C_i$ which meet the 0.15 significance level were entered into the model.
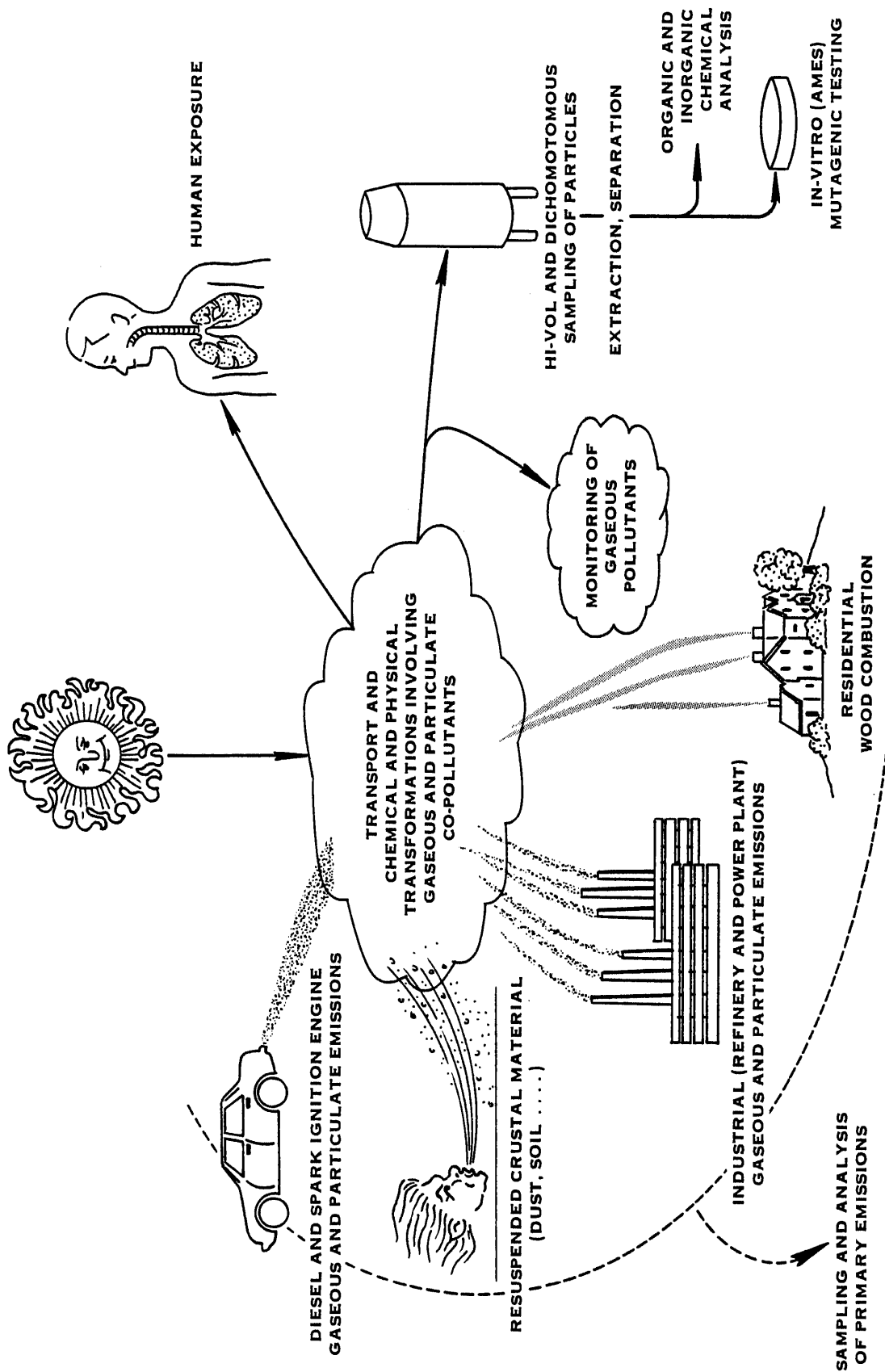
FIGURE 13. SOURCES OF GASEOUS AND PARTICULATE AIR POLLUTANTS: CHEMICAL AND PHYSICAL TRANSFORMATIONS INVOLVING TRANSPORT IN THE ATMOSPHERE AND DURING THE SAMPLING, MAKE SOURCE IDENTIFICATION DIFFICULT.

# IV. INTENSIVE SAMPLING FOR MUTAGEN SOURCE IDENTIFICATION DURING THREE SEASONAL POLLUTION EPISODES

As described above, intensive air sampling for mutagen source identification was carried out during three 36 hour pollution episodes in 1981-82. During the August 6-7, 1981 episode, one 12 hour night and two 12 hour day periods were sampled. Light westerly breezes prevailed throughout the sampling period. The base of the inversion was ca. 200m by night, decreasing further during daytime sampling. This episode contained the third "dirtiest" day of the year, according to the BAAQMD Pollution Standards Index (36).

During the October 20-22, 1982 episode, one day and two nighttime periods were sampled. Winds were light and from the northeast aloft during the first nights' sampling; the inversion base was ca. 400m. The following day, weak westerly sea breezes prevailed and the base of the inversion dropped to ca. 160m. During the second night, the wind direction reversed while the inversion base remained below 200m.

In the January 13-15, 1982 episode, one day and two nighttime periods were sampled. This third episode was characterized by a moderately strong northeasterly gradient. Pollutant levels increased during the night as the base of a strong inversion dropped to sea level. During the day there was a moderate clean-out as the inversion base lifted to about 100m.

For each episode, hi-vol and dichotomous size-segregated particulate samples were collected over three consecutive 12 hour periods (0600-1800; 1800-0600) at the three permanent stations (Richmond, Concord, Pittsburg) and the one temporary location (Mountain View Sanitary District Facility, Martinez). Gaseous pollutants were measured at the three permanent stations but not at Martinez. The meteorological information for the study days was derived from data collected at the Oakland airport. Meteorological data permitted qualitative descriptions of the episodes but were too limited for use in quantitative analysis.

Because of instrument malfunctions, no hi-vol or dichotomous samples for suspended particulate mass variables (TSP, IP, etc.), Sulfate ($SO_4^=$), Nitrate ($NO_3^-$), benzene soluble organics (BSO) and the trace elements were obtained at Concord

during the first 12-hour period in October. Also no dichotomous samples for mass and trace element variables were collected at Pittsburg during the winter episode.

During the fall and winter episode, mutagenic responses were determined in strains TA98 and TA98NR, both with and without rat liver (S9) proteins. Because of limited amounts of sample, summer episode extracts were tested in TA98+S9 and TA98NR-S9 only. Both strains respond mainly to frame-shift mutagens. Direct-acting mutagens are detected without S9. Both indirect- and direct-acting mutagens are detected in the presence of S9, although the activities of some direct-acting chemicals are decreased by the addition of S9 (24). Thus, the term "Total Indirect" mutagenicity operationally defines the response of the Ames test in the presence of S9. Strain TA98NR is deficient in the classical nitroreductase which is used by <u>Salmonella</u> to activate a variety of nitroorganic mutagens, among which are 1-$NO_2$pyrene and 2-$NO_2$fluorene (28,29). Decreased activity of air extracts in TA98NR relative to TA98 suggests the presence of nitroarenes such as 1-$NO_2$pyrene. However some nitroarenes, notably 1,6-and 1,8-dinitropyrene, are highly mutagenic in both TA98 and TA98NR. These dinitro compounds employ a different nitroreductase for activation. Thus, the response in TA98NR is not independant of contributions from nitroarenes such as 1,6-and 1,8-dinitropyrene.

Some pollutant variables were more useful than others for interpretation of episode source patterns. They included those particulate and gas pollutants and mutagenic variables defined in Table 2. Summary statistics (means, standard deviations, maxima and minima) for these variables by episode and by station are shown in Tables 8-14. In determining episode means, consideration was given to the differences in sampling patterns during the episodes. That is, during the summer episode one night time and two day time samples were collected while during the fall and winter episodes, one day and two night samples were collected. In order to determine means and other statistical parameters based on equal periods of day time and night time sampling, results of the single sampling period were introduced twice to create a "dummy" data set.

Two types of mutagenic concentrations were used for interpretation. "Mutagenic Density" (revertants per $m^3$) measures potential human exposure through inhalation to chemicals detected by the Ames test. "Specific Activity", or "Mutagenic

TABLE 8

SUMMARY STATISTICS
AUGUST 6-7, 1981 EPISODE (I)

| Variable | Units | N | Mean | Standard Deviation | Minimum Value | Maximum Value |
|---|---|---|---|---|---|---|
| TSP | $\mu G/M^3$ | 16 | 81 | 44 | 23 | 213 |
| FDCX | $\mu G/M^3$ | 16 | 14 | 5 | 7 | 24 |
| CDCX | $\mu G/M^3$ | 16 | 25 | 16 | 5 | 75 |
| IP | $\mu G/M^3$ | 16 | 39 | 19 | 12 | 92 |
| IP/TSP | | 16 | 0.50 | 0.08 | 0.23 | 0.57 |
| SO$_4$ | $\mu G/M^3$ | 16 | 12.3 | 5.3 | 3.7 | 19.4 |
| NO$_3$ | $\mu G/M^3$ | 16 | 6.4 | 3.6 | 1.7 | 12.3 |
| BSO | $\mu G/M^3$ | 16 | 3.3 | 1.4 | 1.4 | 6.3 |
| CHR | $NG/M^3$ | 16 | 0.1 | 0.08 | < 0.1 | 0.4 |
| BAP | $NG/M^3$ | 16 | < 0.1 | 0.0 | < 0.1 | < 0.1 |
| BGP | $NG/M^3$ | 16 | 0.6 | 0.3 | 0.2 | 1.0 |
| COR | $NG/M^3$ | 16 | 0.4 | 0.2 | < 0.1 | 0.6 |
| BO | $NG/M^3$ | 16 | 0.4 | 0.2 | < 0.1 | 0.8 |
| PAH* | $NG/M^3$ | 16 | 2.2 | 0.8 | 0.9 | 3.2 |
| IRON | $NG/M^3$ | 16 | 1126 | 817 | 143 | 3568 |
| NICKEL | $NG/M^3$ | 16 | 33 | 16 | 13 | 59 |
| ZINC | $NG/M^3$ | 16 | 64 | 33 | 12 | 147 |
| BROM | $NG/M^3$ | 16 | 39 | 18 | 15 | 68 |
| DC LEAD | $NG/M^3$ | 16 | 208 | 97 | 53 | 371 |
| BR/PB | | 16 | 0.20 | 0.04 | 0.12 | 0.28 |
| | | | | | | |
| M398PS9 | $REV/M^3$ | 16 | 14.7 | 7.9 | 1.3 | 30.0 |
| M398MS9 | $REV/M^3$ | 16 | 6.6 | 3.5 | 0.8 | 12.4 |
| M398NRM | $REV/M^3$ | 16 | 1.5 | 0.6 | 0.2 | 2.7 |
| NR/98M3 | | 16 | 0.26 | 0.11 | 0.15 | 0.63 |
| BSO98PS9 | $REV/\mu G$ | 16 | 4.0 | 2.4 | 0.9 | 8.5 |
| BSO98MS9 | $REV/\mu G$ | 16 | 2.1 | 1.2 | 0.6 | 4.4 |
| BSO98NRM | $REV/\mu G$ | 14 | 0.5 | 0.2 | 0.2 | 1.0 |
| NR/98BSO | | 14 | 0.25 | 0.06 | 0.15 | 0.36 |
| | | | | | | |
| O$_3$ | PPHM | 12 | 3.3 | 2.2 | 0.8 | 6.8 |
| CO | PPM | 12 | 0.76 | 0.30 | 0.20 | 1.0 |
| NO$_2$ | PPHM | 12 | 3.1 | 1.7 | 0.3 | 5.1 |
| NO | PPHM | 12 | 1.0 | 0.6 | < 0.05 | 1.9 |
| SO$_2$ | PPHM | 12 | 0.42 | 0.40 | < 0.05 | 1.0 |

*In Tables 8-14, PAH is the sum of the eight unsubstituted PAH and one carbonyl PAH derivative, benzanthrone, which are listed in Table 2.

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TABLE 9

SUMMARY STATISTICS
OCTOBER 20-22, 1981 EPISODE (II)

| Variable | Units | N | Mean | Standard Deviation | Minimum Value | Maximum Value |
|---|---|---|---|---|---|---|
| TSP | $\mu G/M^3$ | 15 | 101 | 28 | 39 | 142 |
| FDCX | $\mu G/M^3$ | 15 | 37 | 10 | 18 | 49 |
| CDCX | $\mu G/M^3$ | 15 | 20 | 6 | 7 | 28 |
| IP | $\mu G/M^3$ | 15 | 57 | 14 | 25 | 73 |
| IP/TSP | | 15 | 0.58 | 0.08 | 0.48 | 0.72 |
| SO$_4$ | $\mu G/M^3$ | 15 | 18.4 | 6.3 | 6.1 | 27.4 |
| NO$_3$ | $\mu G/M^3$ | 15 | 15.1 | 5.1 | 4.2 | 21.1 |
| BSO | $\mu G/M^3$ | 15 | 10.0 | 2.4 | 5.6 | 13.9 |
| CHR | $NG/M^3$ | 16 | 0.3 | 0.2 | < 0.1 | 1.0 |
| BAP | $NG/M^3$ | 16 | 0.4 | 0.40 | < 0.1 | 1.5 |
| BGP | $NG/M^3$ | 16 | 1.5 | 1.4 | 0.4 | 5.1 |
| COR | $NG/M^3$ | 16 | 0.9 | 0.7 | 0.2 | 2.6 |
| BO | $NG/M^3$ | 16 | 1.4 | 1.0 | 0.4 | 3.8 |
| PAH | $NG/M^3$ | 16 | 5.6 | 4.4 | 1.6 | 17.3 |
| IRON | $NG/M^3$ | 15 | 914 | 376 | 195 | 1427 |
| NICKEL | $NG/M^3$ | 15 | 36 | 18 | 14 | 76 |
| ZINC | $NG/M^3$ | 15 | 99 | 84 | 15 | 290 |
| BROM | $NG/M^3$ | 15 | 97 | 61 | 26 | 279 |
| DC LEAD | $NG/M^3$ | 15 | 400 | 232 | 94 | 1036 |
| BR/PB | | 15 | 0.24 | 0.02 | 0.21 | 0.29 |
| | | | | | | |
| M398PS9 | $REV/M^3$ | 16 | 11.3 | 7.0 | 4.3 | 27.3 |
| M398MS9 | $REV/M^3$ | 16 | 7.2 | 3.3 | 1.0 | 14.0 |
| M398NRM | $REV/M^3$ | 16 | 3.7 | 1.3 | 1.1 | 6.9 |
| NR/98M3 | | 16 | 0.57 | 0.20 | 0.34 | 1.10 |
| BSO98PS9 | $REV/\mu G$ | 15 | 1.0 | 0.4 | 0.4 | 1.9 |
| BSO98MS9 | $REV/\mu G$ | 15 | 0.7 | 0.2 | 0.2 | 1.0 |
| BSO98NRM | $REV/\mu G$ | 15 | 0.3 | 0.1 | 0.2 | 0.5 |
| NR/98BSO | | 15 | 0.6 | 0.2 | 0.3 | 1.1 |
| | | | | | | |
| O$_3$ | PPHM | 11 | 1.5 | 1.2 | < 0.05 | 3.4 |
| CO | PPM | 12 | 1.4 | 0.6 | 0.6 | 2.7 |
| NO$_2$ | PPHM | 12 | 4.6 | 1.6 | 1.2 | 6.4 |
| NO | PPHM | 12 | 3.0 | 3.2 | 0.1 | 9.9 |
| SO$_2$ | PPHM | 12 | 0.35 | 0.27 | < 0.05 | 0.80 |

TABLE 10

SUMMARY STATISTICS
JANUARY 13-15, 1982 EPISODE (III)

| Variable | Units | N | Mean | Standard Deviation | Minimum Value | Maximum Value |
|----------|-------|---|------|--------------------|---------------|---------------|
| TSP | $\mu G/M^3$ | 16 | 90 | 15 | 57 | 112 |
| FDCX | $\mu G/M^3$ | 12 | 41 | 8 | 31 | 55 |
| CDCX | $\mu G/M^3$ | 12 | 15 | 6 | 8 | 25 |
| IP | $\mu G/M^3$ | 12 | 56 | 11 | 44 | 80 |
| IP/TSP | | 12 | 0.58 | 0.09 | 0.48 | 0.71 |
| $SO_4$ | $\mu G/M^3$ | 16 | 13.9 | 6.1 | 4.6 | 22.6 |
| $NO_3$ | $\mu G/M^3$ | 16 | 13.3 | 2.8 | 8.8 | 18.7 |
| BSO | $\mu G/M^3$ | 16 | 8.9 | 3.2 | 4.8 | 16.5 |
| CHR | $NG/M^3$ | 16 | 1.1 | 0.8 | 0.4 | 2.6 |
| BAP | $NG/M^3$ | 16 | 1.1 | 0.9 | 0.2 | 2.6 |
| BGP | $NG/M^3$ | 16 | 2.2 | 1.1 | 0.5 | 4.6 |
| COR | $NG/M^3$ | 16 | 1.0 | 0.5 | 0.2 | 2.1 |
| BO | $NG/M^3$ | 16 | 4.5 | 2.5 | 1.4 | 9.5 |
| PAH | $NG/M^3$ | 16 | 13.8 | 7.5 | 4.1 | 28.6 |
| IRON | $NG/M^3$ | 12 | 499 | 371 | 96 | 1269 |
| NICKEL | $NG/M^3$ | 12 | 26 | 7 | 20 | 36 |
| ZINC | $NG/M^3$ | 12 | 58 | 15 | 37 | 82 |
| BROM | $NG/M^3$ | 11 | 117 | 21 | 74 | 150 |
| DC LEAD | $NG/M^3$ | 11 | 359 | 69 | 223 | 479 |
| BR/PB | | 11 | 0.33 | 0.06 | 0.28 | 0.43 |
| | | | | | | |
| M398PS9 | $REV/M^3$ | 16 | 9.0 | 3.4 | 4.3 | 15.7 |
| M398MS9 | $REV/M^3$ | 16 | 6.7 | 2.2 | 3.5 | 11.8 |
| M398NRM | $REV/M^3$ | 16 | 3.4 | 1.4 | 1.5 | 6.2 |
| NR/98M3 | | 16 | 0.51 | 0.13 | 0.25 | 0.73 |
| BSO98PS9 | $REV/\mu G$ | 16 | 1.1 | 0.6 | 0.4 | 2.1 |
| BSO98MS9 | $REV/\mu G$ | 16 | 0.8 | 0.3 | 0.4 | 1.4 |
| BSO98NRM | $REV/\mu G$ | 16 | 0.4 | 0.2 | 0.2 | 0.8 |
| NR/98BSO | | 16 | 0.51 | 0.13 | 0.26 | 0.73 |
| | | | | | | |
| $O_3$ | PPHM | 12 | 0.2 | 0.3 | < 0.05 | 0.6 |
| CO | PPM | 12 | 1.6 | 0.4 | 1.0 | 2.2 |
| $NO_2$ | PPHM | 12 | 3.2 | 0.6 | 2.2 | 4.1 |
| NO | PPHM | 12 | 4.2 | 2.0 | 1.8 | 7.8 |
| $SO_2$ | PPHM | 12 | 0.31 | 0.43 | < 0.05 | 1.10 |

TABLE 11

SUMMARY STATISTICS
PITTSBURG STATION – THREE EPISODES

| Variable | Units | N | Mean | Standard Deviation | Minimum Value | Maximum Value |
|---|---|---|---|---|---|---|
| TSP | $\mu G/M^3$ | 12 | 83 | 18 | 57 | 106 |
| FDCX | $\mu G/M^3$ | 8 | 23 | 12 | 12 | 41 |
| CDCX | $\mu G/M^3$ | 8 | 24 | 6 | 17 | 35 |
| IP | $\mu G/M^3$ | 8 | 47 | 10 | 32 | 60 |
| IP/TSP | | 8 | 0.53 | 0.07 | 0.45 | 0.65 |
| $SO_4$ | $\mu G/M^3$ | 12 | 12.7 | 6.3 | 4.6 | 23.8 |
| $NO_3$ | $\mu G/M^3$ | 12 | 12.9 | 5.5 | 5.0 | 21.1 |
| BSO | $\mu G/M^3$ | 12 | 6.8 | 3.1 | 2.4 | 10.0 |
| CHR | $NG/M^3$ | 12 | 0.5 | 0.4 | < 0.1 | 1.3 |
| BAP | $NG/M^3$ | 12 | 0.4 | 0.4 | < 0.1 | 1.3 |
| BGP | $NG/M^3$ | 12 | 1.1 | 0.5 | 0.4 | 1.9 |
| COR | $NG/M^3$ | 12 | 0.7 | 0.1 | 0.4 | 0.8 |
| BO | $NG/M^3$ | 12 | 2.0 | 2.3 | 0.4 | 7.1 |
| PAH | $NG/M^3$ | 12 | 6.2 | 4.9 | 1.8 | 16.5 |
| IRON | $NG/M^3$ | 8 | 1133 | 401 | 758 | 1806 |
| NICKEL | $NG/M^3$ | 8 | 30 | 8 | 19 | 41 |
| ZINC | $NG/M^3$ | 8 | 144 | 91 | 79 | 290 |
| BROM | $NG/M^3$ | 8 | 71 | 33 | 31 | 105 |
| DC LEAD | $NG/M^3$ | 8 | 334 | 130 | 153 | 455 |
| BR/PB | | 8 | 0.21 | 0.03 | 0.16 | 0.24 |
| | | | | | | |
| M398PS9 | $REV/M^3$ | 12 | 12.3 | 4.6 | 7.0 | 21.8 |
| M398MS9 | $REV/M^3$ | 12 | 8.6 | 2.1 | 5.9 | 12.4 |
| M398NRM | $REV/M^3$ | 12 | 2.9 | 1.6 | 1.3 | 6.2 |
| NR/98M3 | | 12 | 0.33 | 0.14 | 0.15 | 0.57 |
| BSO98PS9 | $REV/\mu G$ | 12 | 2.6 | 2.2 | 0.9 | 5.7 |
| BSO98MS9 | $REV/\mu G$ | 12 | 1.6 | 1.0 | 0.7 | 3.7 |
| BSO98NRM | $REV/\mu G$ | 12 | 0.4 | 0.2 | 0.2 | 0.8 |
| NR/98BSO | | 12 | 0.33 | 0.14 | 0.15 | 0.57 |
| | | | | | | |
| $O_3$ | PPHM | 12 | 2.0 | 2.4 | < 0.05 | 6.8 |
| CO | PPM | 12 | 1.1 | 0.2 | 1.0 | 1.4 |
| $NO_2$ | PPHM | 12 | 3.7 | 1.2 | 2.2 | 5.3 |
| NO | PPHM | 12 | 1.7 | 0.6 | 1.0 | 2.4 |
| $SO_2$ | PPHM | 12 | 0.48 | 0.41 | < 0.05 | 1.0 |

TABLE 12

SUMMARY STATISTICS
RICHMOND STATION - THREE EPISODES

| Variable | Units | N | Mean | Standard Deviation | Minimum Value | Maximum Value |
|----------|-------|---|------|--------------------|---------------|---------------|
| TSP | $\mu G/M^3$ | 12 | 75 | 35 | 23 | 111 |
| FDCX | $\mu G/M^3$ | 12 | 25 | 16 | 7 | 54 |
| CDCX | $\mu G/M^3$ | 12 | 14 | 6 | 5 | 20 |
| IP | $\mu G/M^3$ | 12 | 39 | 20 | 12 | 74 |
| IP/TSP | | 12 | 0.54 | 0.12 | 0.22 | 0.72 |
| $SO_4$ | $\mu G/M^3$ | 12 | 11.7 | 5.8 | 3.7 | 19.9 |
| $NO_3$ | $\mu G/M^3$ | 12 | 7.9 | 4.1 | 1.7 | 14.5 |
| BSO | $\mu G/M^3$ | 12 | 6.1 | 3.5 | 1.4 | 12.1 |
| CHR | $NG/M^3$ | 12 | 0.5 | 0.8 | < 0.1 | 2.6 |
| BAP | $NG/M^3$ | 12 | 0.6 | 0.9 | < 0.1 | 2.6 |
| BGP | $NG/M^3$ | 12 | 1.5 | 1.5 | 0.2 | 4.6 |
| COR | $NG/M^3$ | 12 | 0.8 | 0.6 | < 0.1 | 2.1 |
| BO | $NG/M^3$ | 12 | 2.4 | 2.7 | < 0.1 | 7.7 |
| PAH | $\mu G/M^3$ | 12 | 7.8 | 9.0 | 0.9 | 28.6 |
| IRON | $NG/M^3$ | 12 | 688 | 407 | 143 | 1269 |
| NICKEL | $NG/M^3$ | 12 | 20 | 7 | 13 | 35 |
| ZINC | $NG/M^3$ | 12 | 55 | 35 | 12 | 109 |
| BROM | $NG/M^3$ | 12 | 68 | 47 | 15 | 150 |
| DC LEAD | $NG/M^3$ | 12 | 261 | 157 | 53 | 479 |
| BR/PB | | 12 | 0.26 | 0.04 | 0.18 | 0.31 |
| | | | | | | |
| M398PS9 | $REV/M^3$ | 12 | 9.2 | 5.1 | 1.3 | 15.7 |
| M398MS9 | $REV/M^3$ | 12 | 5.3 | 3.4 | 0.8 | 11.8 |
| M398NRM | $REV/M^3$ | 12 | 2.7 | 1.8 | 0.2 | 5.6 |
| NR/98M3 | | 12 | 0.56 | 0.26 | 0.24 | 1.10 |
| BSO98PS9 | $REV/\mu G$ | 12 | 1.9 | 1.8 | 0.8 | 6.2 |
| BSO98MS9 | $REV/\mu G$ | 12 | 1.0 | 0.6 | 0.2 | 2.3 |
| BSO98NRM | $REV/\mu G$ | 10 | 0.5 | 0.2 | 0.2 | 0.8 |
| NR/98BSO | | 10 | 0.6 | 0.3 | 0.3 | 1.1 |
| | | | | | | |
| $O_3$ | PPHM | 12 | 1.6 | 1.1 | < 0.05 | 2.8 |
| CO | PPM | 12 | 1.1 | 0.6 | 0.2 | 2.2 |
| $NO_2$ | PPHM | 12 | 2.5 | 1.4 | 0.3 | 4.1 |
| NO | PPHM | 12 | 2.4 | 2.6 | < 0.05 | 7.8 |
| $SO_2$ | PPHM | 12 | 0.07 | 0.10 | < 0.05 | 0.30 |

## TABLE 13

### SUMMARY STATISTICS
### MARTINEZ STATION* — THREE EPISODES

| Variable | Units | N | Mean | Standard Deviation | Minimum Value | Maximum Value |
|---|---|---|---|---|---|---|
| TSP | $\mu G/M^3$ | 12 | 111 | 40 | 71 | 213 |
| FDCX | $\mu G/M^3$ | 12 | 34 | 13 | 16 | 48 |
| CDCX | $\mu G/M^3$ | 12 | 26 | 18 | 8 | 75 |
| IP | $\mu G/M^3$ | 12 | 60 | 16 | 39 | 92 |
| IP/TSP | | 12 | 0.56 | 0.08 | 0.43 | 0.70 |
| $SO_4$ | $\mu G/M^3$ | 12 | 21.4 | 3.4 | 16.9 | 27.4 |
| $NO_3$ | $\mu G/M^3$ | 12 | 12.8 | 5.5 | 3.2 | 19.2 |
| BSO | $\mu G/M^3$ | 12 | 8.1 | 2.7 | 4.2 | 11.5 |
| CHR | $NG/M^3$ | 12 | 0.3 | 0.4 | < 0.1 | 1.2 |
| BAP | $NG/M^3$ | 12 | 0.4 | 0.4 | < 0.1 | 1.5 |
| BGP | $NG/M^3$ | 12 | 0.7 | 0.5 | 0.4 | 2.1 |
| COR | $NG/M^3$ | 12 | 0.4 | 0.2 | 0.2 | 0.8 |
| BO | $NG/M^3$ | 12 | 1.4 | 1.8 | 0.2 | 5.7 |
| PAH | $NG/M^3$ | 12 | 4.3 | 4.1 | 1.4 | 16.1 |
| IRON | $NG/M^3$ | 12 | 995 | 966 | 96 | 3568 |
| NICKEL | $NG/M^3$ | 12 | 44 | 20 | 20 | 76 |
| ZINC | $NG/M^3$ | 12 | 60 | 31 | 33 | 147 |
| BROM | $NG/M^3$ | 11 | 64 | 39 | 24 | 133 |
| DC LEAD | $NG/M^3$ | 11 | 228 | 62 | 128 | 310 |
| BR/PB | | 11 | 0.26 | 0.10 | 0.12 | 0.43 |
| | | | | | | |
| M398PS9 | $REV/M^3$ | 12 | 7.8 | 4.4 | 4.3 | 17.3 |
| M398MS9 | $REV/M^3$ | 12 | 5.2 | 1.6 | 3.5 | 7.3 |
| M398NRM | $REV/M^3$ | 12 | 2.3 | 1.0 | 1.2 | 4.4 |
| NR/98M3 | | 12 | 0.45 | 0.15 | 0.21 | 0.63 |
| BSO98PS9 | $REV/\mu G$ | 12 | 1.1 | 0.8 | 0.4 | 2.7 |
| BSO98MS9 | $REV/\mu G$ | 12 | 0.7 | 0.2 | 0.4 | 1.0 |
| BSO98NRM | $REV/\mu G$ | 12 | 0.3 | 0.1 | 0.2 | 0.4 |
| NR/98BSO | | 12 | 0.45 | 0.15 | 0.20 | 0.63 |

*No gas pollutants measured

TABLE 14

SUMMARY STATISTICS
CONCORD STATION - THREE EPISODES

| Variable | Units | N | Mean | Standard Deviation | Minimum Value | Maximum Value |
|----------|-------|---|------|--------------------|---------------|----------------|
| TSP | $\mu G/M^3$ | 11 | 93 | 18 | 63 | 112 |
| FDCX | $\mu G/M^3$ | 11 | 34 | 15 | 15 | 55 |
| CDCX | $\mu G/M^3$ | 11 | 19 | 6 | 8 | 30 |
| IP | $\mu G/M^3$ | 11 | 53 | 14 | 34 | 80 |
| IP/TSP | | 11 | 0.57 | 0.07 | 0.48 | 0.71 |
| $SO_4$ | $\mu G/M^3$ | 11 | 13.3 | 4.4 | 3.7 | 18.9 |
| $NO_3$ | $\mu G/M^3$ | 11 | 12.5 | 5.2 | 4.4 | 19.6 |
| BSO | $\mu G/M^3$ | 11 | 8.3 | 5.6 | 2.7 | 16.5 |
| CHR | $NG/M^3$ | 12 | 0.8 | 0.8 | < 0.1 | 2.6 |
| BAP | $NG/M^3$ | 12 | 0.9 | 0.9 | < 0.1 | 2.6 |
| BGP | $NG/M^3$ | 12 | 2.3 | 1.4 | 0.7 | 5.1 |
| COR | $NG/M^3$ | 12 | 1.2 | 0.7 | 0.6 | 2.6 |
| BO | $NG/M^3$ | 12 | 2.6 | 2.5 | 0.4 | 9.5 |
| PAH | $NG/M^3$ | 12 | 10.4 | 7.9 | 2.5 | 27.2 |
| IRON | $NG/M^3$ | 11 | 769 | 421 | 158 | 1549 |
| NICKEL | $NG/M^3$ | 11 | 34 | 6 | 26 | 46 |
| ZINC | $NG/M^3$ | 11 | 62 | 15 | 39 | 89 |
| BROM | $NG/M^3$ | 11 | 116 | 64 | 52 | 279 |
| DC LEAD | $NG/M^3$ | 11 | 451 | 225 | 308 | 1036 |
| BR/PB | | 11 | 0.26 | 0.07 | 0.16 | 0.39 |
| | | | | | | |
| M398PS9 | $REV/M^3$ | 12 | 17.5 | 8.1 | 6.9 | 30.0 |
| M398MS9 | $REV/M^3$ | 12 | 8.4 | 3.0 | 5.4 | 14.0 |
| M398NRM | $REV/M^3$ | 12 | 3.6 | 1.5 | 2.0 | 6.9 |
| NR/98M3 | | 12 | 0.45 | 0.17 | 0.21 | 0.73 |
| BSO98PS9 | $REV/\mu G$ | 11 | 2.7 | 2.6 | 0.4 | 8.5 |
| BSO98MS9 | $REV/\mu G$ | 11 | 1.6 | 1.4 | 0.4 | 4.4 |
| BSO98NRM | $REV/\mu G$ | 11 | 0.5 | 0.2 | 0.2 | 0.7 |
| NR/98BSO | | 11 | 0.45 | 0.17 | 0.20 | 0.73 |
| | | | | | | |
| $O_3$ | PPHM | 11 | 1.5 | 2.2 | < 0.05 | 6.0 |
| CO | PPM | 12 | 1.5 | 0.7 | 0.6 | 2.7 |
| $NO_2$ | PPHM | 12 | 4.7 | 1.2 | 3.0 | 6.4 |
| NO | PPHM | 12 | 4.2 | 3.0 | 0.8 | 9.9 |
| $SO_2$ | PPHM | 12 | 0.53 | 0.33 | 0.20 | 1.10 |

Loading", measures revertants per ug BSO (or TSP) and thus gives the concentration of substances active in the Ames test on a mass basis.

A.   Summary Statistics: Episode, Station and Diurnal Comparisons in TA98 and TA98NR.

Episodes

Episode Comparisons Are Summarized in Tables 8-10. Total suspended particulate mass concentrations were fairly constant during the three episodes, varying by only twenty percent from a low of 81 ug/m$^3$ in the summer episode (I) to a high of 101 ug/m$^3$ in the fall episode (II). Somewhat higher levels of inhalable particle (<15 um) were measured October (60 ug/m$^3$) and January (56 ug/m$^3$) than in August (39 ug/m$^3$). This was due to higher fine particle (d $\leq$2.5 um) loadings during the fall and winter episodes.

Like TSP, mean $SO_4^=$ concentrations were also approximately constant, ranging from a low of 12 ug/m$^3$ in August to a high of 18 ug/m$^3$ in October. $SO_4^=$ is derived from $SO_2$ emitted primarily by industrial sources (petroleum refining, chemical manufacture, electrical generation) in Contra Costa County (36).

The mean $NO_3^-$ concentration in August (6 ug/m$^3$) was lower by more than a factor of two than those in October (13 ug/m$^3$) and January (15 ug/m$^3$). $NO_3^-$ is a secondary pollutant derived predominantly from atmospheric transformations of gaseous NO and $NO_2$. In Contra Costa County, emission inventories indicate that about one quarter of the oxides of nitrogen (NOx) are derived from mobile sources and about three quarters from stationary sources. Particulate $NO_3^-$ concentrations measured on Hi-vol samples contain positive artifacts due to gas phase nitric acid (38). Also, possible contributions from large particles (e.g., fertilizer) were not excluded. Thus $NO_3^-$ interpretation is complex.

Among organic pollutants, episode by episode variations were even more dramatic. Concentrations of total organics (BSO) were 2-3 times higher in fall and winter than in summer. Among individual PAH, coronene exhibited the smallest variation from episode to episode, only a factor of two, but

chrysene, benz(a)pyrene and benzanthrone were all at least ten times more concentrated in January than in August.

In contrast to these organic variables, mutagenic densities (concentrations in revertants per $m^3$) did not vary greatly by episode. Among mutagens active in the presence of S9, the highest mean value was in summer (15 rev/$m^3$; + S9) and lowest in winter (9 rev/$m^3$; + S9). Addition of S9 increased the mutagenic activity of extracts from all three episodes, but to different extents. Thus both direct and indirect acting mutagens are present. The concentration of direct-acting mutagens were remarkably constant for the three episodes (6.6, 7.2, 6.7 rev/$m^3$ respectively). Mutagenic specific activities (revertants per ug organic extractables) were however 3-4 times higher in August than in January. October values were intermediate. The higher specific activity mutagens present in the summer episode may result partially from atmospheric transformations; alternatively, loading the atmosphere with organic components of low specific mutagenicity (e.g., wood-combustion products) in the winter may be the reason for the episode differences.

Three trace metals were especially useful for source reconciliation. These were lead (Pb), Nickel (Ni) and iron (Fe). The episode mean values for the three trace metals measured on dichotomous filter samples varied as follows: Pb from 0.2 ug/$m^3$ in August to 0.4 ug/$m^3$ in October; Fe from 0.5 ug/$m^3$ in January to 1.1 ug/$m^3$ in August; Ni from 26 ng/$m^3$ in January to 36 ng/$m^3$ in October. We have applied the conclusions of Cass and McRae (36) for the South Coast Air Basin to Contra Costa aerosols. Most Pb emissions are assumed to come from highway traffic, most nickel from fuel oil fly ash and most iron from resuspended crustal material. Throughout the present analysis, Pb was used as source-related descriptors of transportation and Ni as a descriptor of industry. $SO_4$ and $NO_3$ were used as secondary aerosol descriptors.

Among the gases, ozone showed the greatest episode variations; concentrations were 10 times higher in August than in January. In contrast to the behavior of ozone, NO was 3-4 times higher in fall and winter episodes

than in the summer episode.  The episode mean concentrations of the other measured gases (CO, $NO_2$, $SO_2$) varied by less than a factor of two.

## Station Comparisons

Station-by-station comparisons are shown in Tables 11-14.  Nickel was present in highest concentration in air samples collected at the Mountain View Sanitary District Facility, Martinez, which is adjacent to a major petro-chemical refinery complex.   $SO_4^=$ concentrations were also highest at Martinez.  Several particulate pollutants associated with automobile emissions (Pb, coronene) were found in highest concentrations in samples collected at Concord, near the intersection of two busy suburban streets.  The highest mean BAP concentration was also found at Concord (0.85 $ng/m^3$) and the lowest at Martinez and Pittsburg (0.37 and 0.38 $ng/m^3$ respectively).  Mean $NO_3^-$ levels were nearly identical at Pittsburg (12.9 $ug/m^3$), Martinez (12.8 $ug/m^3$) and Concord (12.5 $ug/m^3$) and slightly lower at Richmond (7.9 $ug/m^3$)

Among mutagenic variables, the highest mutagenic densities (revertants/$m^3$) and specific activities (revertants/ug BSO) were measured in samples from Concord and Pittsburg.  Finally, Zn concentrations were more than twice as high at Pittsburg as at the other three stations.  This is consistant with the presence of a significant stationary source of Zn at the Pittsburg Works of U.S. Steel (36).   A possible relationship between Zn and mutagenic emissions is decribed below.

## Diurnal Patterns

Measurements of diurnal patterns are an important technique for assessing sources.  To this end, comparisons of chemical pollutants  and mutagenicity measured separately by day and by night are shown in Tables 15-20.  During the August episode concentrations of most standard particulate pollutants (TSP, Pb, $NO_3^-$ and BSO) were higher by day (Cf Table 15).  Mutagenic densities (revertants/$m^3$) and PAH concentrations were also higher in the day time (Cf Tables 15 and 18).  The August diurnal behavior was especially dramatic at the Richmond Station, which was the upwind site during the

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TABLE 15

MUTAGENIC DENSITY (REV/M³) AND PARTICULATE POLLUTANT CONCENTRATIONS (UG/M³)
IN AIR SAMPLES COLLECTED IN CONTRA COSTA COUNTY, AUGUST 6 - 7, 1981

| Sampling Location | Mutagenic Density -S9 | +S9 | Total Suspended Particulate | Inhalable Particulate | Lead (hi-vol) | Lead (dichot) | Sulfate | Nitrate | Benzene Soluble Organics |
|---|---|---|---|---|---|---|---|---|---|
| Richmond |  |  |  |  |  |  |  |  |  |
| Day | 6.2 | 15.6 | 111 | 25 | 0.25 | 0.20 | 12.6 | 9.8 | 3.0 |
| Night | 0.8 | 1.3 | 23 | 12 | 0.13 | 0.05 | 3.7 | 1.7 | 1.4 |
| Day | 5.0 | 13.2 | 52 | 28 | 0.14 | 0.18 | 9.2 | 3.3 | 2.1 |
| Martinez |  |  |  |  |  |  |  |  |  |
| Day | 5.6 | 16.2 | 118 | 61 | 0.19 | 0.18 | 19.4 | 9.4 | 6.1 |
| Night | 3.6 | 6.9 | 71 | 39 | 0.13 | 0.13 | 19.3 | 3.2 | 4.2 |
| Day | 6.2 | 17.3 | 213 | 92 | 0.29 | 0.22 | 17.5 | 8.9 | 6.3 |
| Concord |  |  |  |  |  |  |  |  |  |
| Day | 12.1 | 30.0 | 88 | 42 | 0.30 | 0.31 | 3.7 | 12.3 | 2.7 |
| Night | 7.3 | 16.9 | 63 | 34 | 0.35 | 0.31 | 11.7 | 4.4 | 3.1 |
| Day | 11.7 | 26.2 | 84 | 48 | 0.27 | 0.38 | 10.5 | 11.5 | 3.1 |
| Pittsburg |  |  |  |  |  |  |  |  |  |
| Day | 9.2 | 21.8 | 100 | 45 | 0.38 | 0.29 | 15.1 | 8.3 | 3.9 |
| Night | 6.9 | 13.2 | 62 | 32 | 0.18 | 0.45 | 12.9 | 5.0 | 2.4 |
| Day | 12.4 | 18.9 | 93 | 48 | 0.29 | 0.30 | 13.7 | 10.7 | 3.3 |

## TABLE 16

### MUTAGENIC DENSITY (REV/M$^3$) AND PARTICULATE POLLUTANT CONCENTRATIONS (UG/M$^3$) IN AIR SAMPLES COLLECTED IN CONTRA COSTA COUNTY, OCTOBER 20 – 22, 1981

| Sampling Location | Mutagenic Density -S9 | +S9 | Total Suspended Particulate | Inhalable Particulate | Lead (hi-vol) | Lead (dichot) | Sulfate | Nitrate | Benzene Soluble Organics |
|---|---|---|---|---|---|---|---|---|---|
| Richmond | | | | | | | | | |
| Night | 1.0 | 4.3 | 39 | 28 | 0.13 | 0.09 | 6.1 | 4.2 | 5.7 |
| Day | 6.2 | 10.2 | 98 | 59 | 0.33 | 0.35 | 19.9 | 10.4 | 8.3 |
| Night | 2.7 | 4.3 | 45 | 25 | 0.13 | 0.15 | 8.4 | 9.5 | 5.6 |
| Martinez | | | | | | | | | |
| Night | 7.3 | 7.5 | 113 | 65 | 0.33 | 0.25 | 27.4 | 15.2 | 11.1 |
| Day | 4.4 | 4.3 | 142 | 73 | 0.33 | 0.26 | 23.6 | 17.0 | 11.4 |
| Night | 6.2 | 7.6 | 107 | 71 | 0.30 | 0.24 | 26.2 | 19.2 | 9.0 |
| Concord | | | | | | | | | |
| Night | 14.0 | 27.3 | * | * | * | * | * | * | * |
| Day | 7.3 | 15.2 | 112 | 57 | 0.59 | 0.62 | 13.2 | 19.6 | 12.7 |
| Night | 10.8 | 26.4 | 102 | 69 | 1.07 | 1.04 | 18.4 | 9.9 | 13.9 |
| Pittsburg | | | | | | | | | |
| Night | 8.9 | 11.3 | 92 | 60 | 0.46 | 0.43 | 21.1 | 14.0 | 10.0 |
| Day | 9.6 | 10.5 | 106 | 51 | 0.42 | 0.45 | 15.8 | 21.1 | 9.8 |
| Night | 10.0 | 11.1 | 94 | 56 | 0.40 | 0.46 | 23.8 | 17.7 | 10.0 |

*Sample missing.

## TABLE 17

### MUTAGENIC DENSITY (REV/M$^3$) AND PARTICULATE POLLUTANT CONCENTRATIONS (UG/M$^3$) IN AIR SAMPLES COLLECTED IN CONTRA COSTA COUNTY, JANUARY 13 - 15, 1982

| Sampling Location | Mutagenic Density -S9 | +S9 | Total Suspended Particulate | Inhalable Particulate | Lead (hi-vol) | Lead (dichot) | Sulfate | Nitrate | Benzene Soluble Organics |
|---|---|---|---|---|---|---|---|---|---|
| **Richmond** | | | | | | | | | |
| Night | 7.5 | 10.0 | 111 | 74 | 0.44 | 0.48 | 11.1 | 14.5 | 12.1 |
| Day | 7.6 | 12.1 | 99 | 48 | 0.38 | 0.41 | 13.8 | 10.2 | 7.5 |
| Night | 11.8 | 15.7 | 101 | 51 | 0.39 | 0.41 | 18.7 | 8.8 | 10.0 |
| **Martinez** | | | | | | | | | |
| Night | 7.1 | 6.1 | 99 | 66 | 0.29 | * | 18.4 | 18.7 | 7.6 |
| Day | 3.5 | 4.3 | 89 | 44 | 0.38 | 0.31 | 22.6 | 14.5 | 7.4 |
| Night | 7.3 | 7.4 | 77 | 54 | 0.30 | 0.22 | 16.9 | 13.0 | 11.5 |
| **Concord** | | | | | | | | | |
| Night | 6.2 | 6.9 | 112 | 80 | 0.40 | 0.36 | 13.2 | 17.8 | 16.5 |
| Day | 5.4 | 9.9 | 94 | 55 | 0.29 | 0.33 | 18.9 | 13.3 | 4.8 |
| Night | 5.7 | 8.8 | 94 | 54 | 0.39 | 0.36 | 13.0 | 11.9 | 14.2 |
| **Pittsburg** | | | | | | | | | |
| Night | 6.5 | 7.0 | 73 | * | 0.29 | * | 4.6 | 14.9 | 6.4 |
| Day | 5.9 | 7.1 | 73 | * | 0.23 | * | 5.9 | 14.0 | 8.1 |
| Night | 10.9 | 15.4 | 57 | * | 0.21 | * | 4.8 | 9.0 | 7.9 |

*Sample missing.

TABLE 18

DIURNAL VARIATIONS IN PARTICULATE PAH* CONCENTRATIONS (NG/M$^3$)
IN CONTRA COSTA AIR SAMPLES COLLECTED AUGUST 6 - 7, 1981

| Sampling Location | CHR | BAA | BBF + BEP | BKF | BAP | BGP | COR | BO + ISO |
|---|---|---|---|---|---|---|---|---|
| **Richmond** | | | | | | | | |
| Day | 0.1 | 0.1 | 0.5 | 0.1 | 0.1 | 0.8 | 0.6 | 0.8 |
| Night | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 |
| Day | 0.1 | 0.1 | 0.4 | 0.1 | 0.1 | 0.7 | 0.5 | 0.7 |
| **Martinez** | | | | | | | | |
| Day | 0.1 | 0.1 | 0.4 | 0.1 | 0.1 | 0.4 | 0.2 | 0.4 |
| Night | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.4 | 0.2 | 0.2 |
| Day | 0.1 | 0.1 | 0.5 | 0.1 | 0.1 | 0.5 | 0.2 | 0.2 |
| **Concord** | | | | | | | | |
| Day | 0.1 | 0.1 | 0.4 | 0.1 | 0.1 | 0.8 | 0.6 | 0.6 |
| Night | 0.1 | 0.1 | 0.4 | 0.1 | 0.1 | 1.0 | 0.6 | 0.4 |
| Day | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.7 | 0.6 | 0.6 |
| **Pittsburg** | | | | | | | | |
| Day | 0.4 | 0.2 | 0.4 | 0.1 | 0.1 | 0.8 | 0.6 | 0.6 |
| Night | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.4 | 0.4 | 0.4 |
| Day | 0.2 | 0.1 | 0.5 | 0.1 | 0.1 | 0.8 | 0.6 | 0.5 |

*Abbreviations used are as follows:  CHR = chrysene, BAA = benz(a)anthracene, BBF + BEP = benzo(b)fluoranthene + benzo(e)pyrene, BKF = benzo(k)flouranthene, BAP = benzo(a)pryrene, BGP = benzo(ghi)perylene, COR = coronene, BO + ISO = benzanthrone + isomers.  Values listed as 0.1 are $\leq$ 0.1.

TABLE 19

DIURNAL VARIATIONS IN PARTICULATE PAH* CONCENTRATIONS (NG/M$^3$)
IN CONTRA COSTA AIR SAMPLES COLLECTED OCTOBER 20 - 22, 1981

| Sampling Location | CHR | BAA | BBF + BEP | BKF | BAP | BGP | COR | BO + ISO |
|---|---|---|---|---|---|---|---|---|
| **Richmond** | | | | | | | | |
| Night | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.4 | 0.2 | 0.4 |
| Day | 0.2 | 0.1 | 0.5 | 0.1 | 0.2 | 0.8 | 0.5 | 1.4 |
| Night | 0.1 | 0.1 | 0.4 | 0.1 | 0.1 | 0.6 | 0.4 | 0.4 |
| **Martinez** | | | | | | | | |
| Night | 0.2 | 0.1 | 0.5 | 0.1 | 0.8 | 0.6 | 0.5 | 0.7 |
| Day | 0.2 | 0.1 | 0.5 | 0.1 | 0.4 | 0.7 | 0.6 | 0.7 |
| Night | 0.1 | 0.1 | 0.4 | 0.1 | 0.1 | 0.5 | 0.4 | 0.8 |
| **Concord** | | | | | | | | |
| Night | 0.6 | 0.5 | 1.7 | 0.5 | 1.1 | 4.2 | 2.3 | 3.8 |
| Day | 0.4 | 0.2 | 1.0 | 0.2 | 0.4 | 2.1 | 1.4 | 1.8 |
| Night | 1.0 | 0.8 | 2.4 | 0.6 | 1.5 | 5.1 | 2.6 | 3.3 |
| **Pittsburg** | | | | | | | | |
| Night | 0.4 | 0.2 | 0.7 | 0.2 | 0.2 | 1.1 | 0.6 | 1.2 |
| Day | 0.2 | 0.1 | 0.7 | 0.2 | 0.2 | 1.4 | 0.8 | 1.3 |
| Night | 0.2 | 0.1 | 0.6 | 0.1 | 0.2 | 0.8 | 0.6 | 1.2 |

*Abbreviations used are as follows:  CHR = chrysene, BAA = benz(a)anthracene, BBF + BEP = benzo(b)fluoranthene + benzo(e)pyrene, BKF = benzo(k)flouranthene, BAP = benzo(a)pyrene, BGP = benzo(ghi)perylene, COR = coronene, BO + ISO = benzanthrone + isomers.  Values listed as 0.1 are $\leq$ 0.1.